HEYROVSKY, Jaroslav 1890 - ed.

Collection des travaux chimiques de Tcecoslovaquie;
Collection of Czech. chem. communications . . . annee 1
Prague, 1929 - Edited and published 1929 by E. Votocsek
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Vol. 1 includes section "Bibliography of Czechoslovakian
chemical publications."

HEYROVSKY, Jaroslav 1890 -

The deposition of radium and other alkaline earth metals at the dropping-mercury cathode. J. Heyrovsky and S. Berezicky. Charles Univ., Prague. Collection Czechoslov. Chem. Comm. 1, 19-45 (1929)

HEYROVSKY, Jaroslav 1890 -

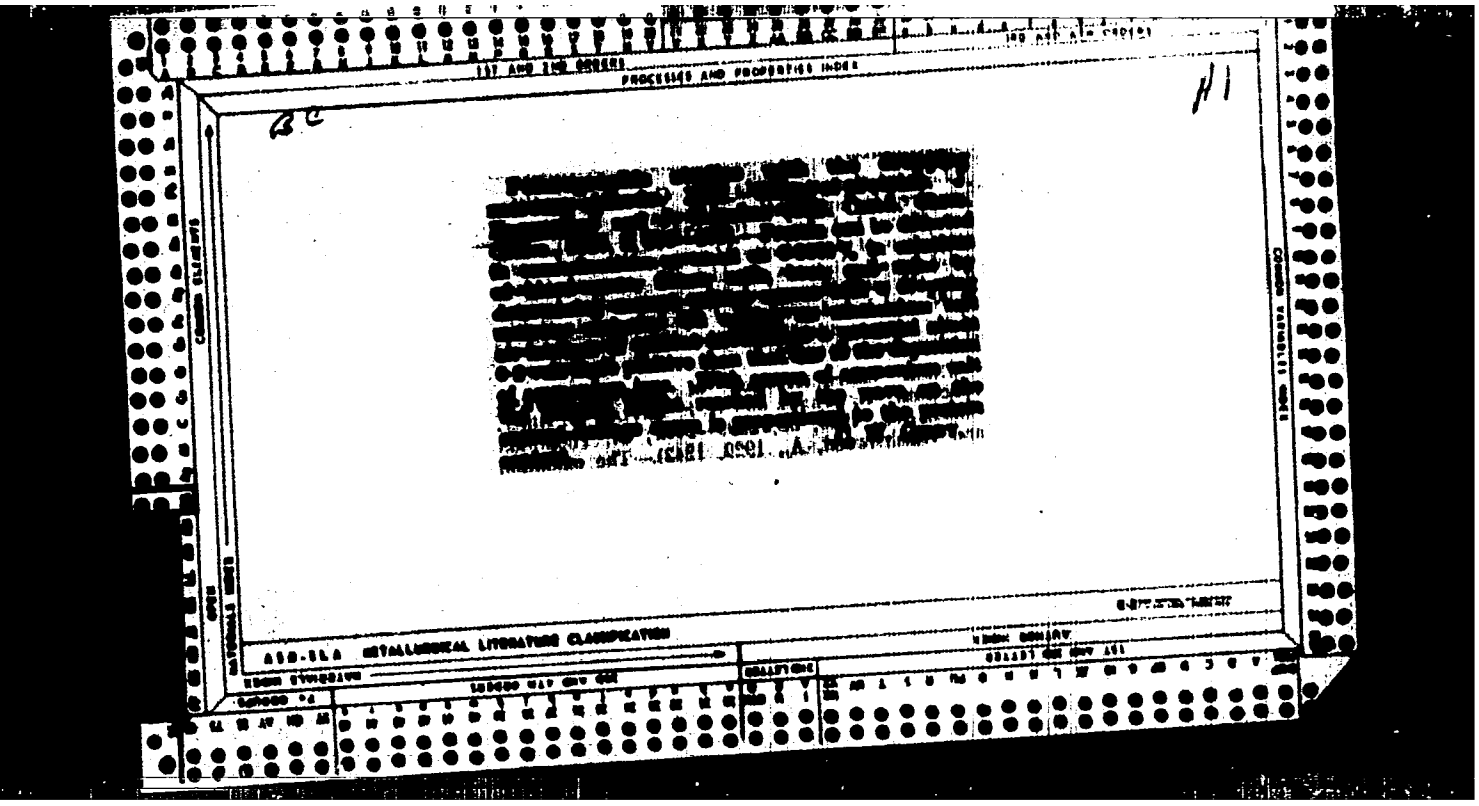
Electrolysis with mercury cathode. II. Explanation of the anomalies on the electro-capillary curves. J. Heyrovsky and R. Simunek. Phil. Mag. (7), 7, 951-70 (1929)

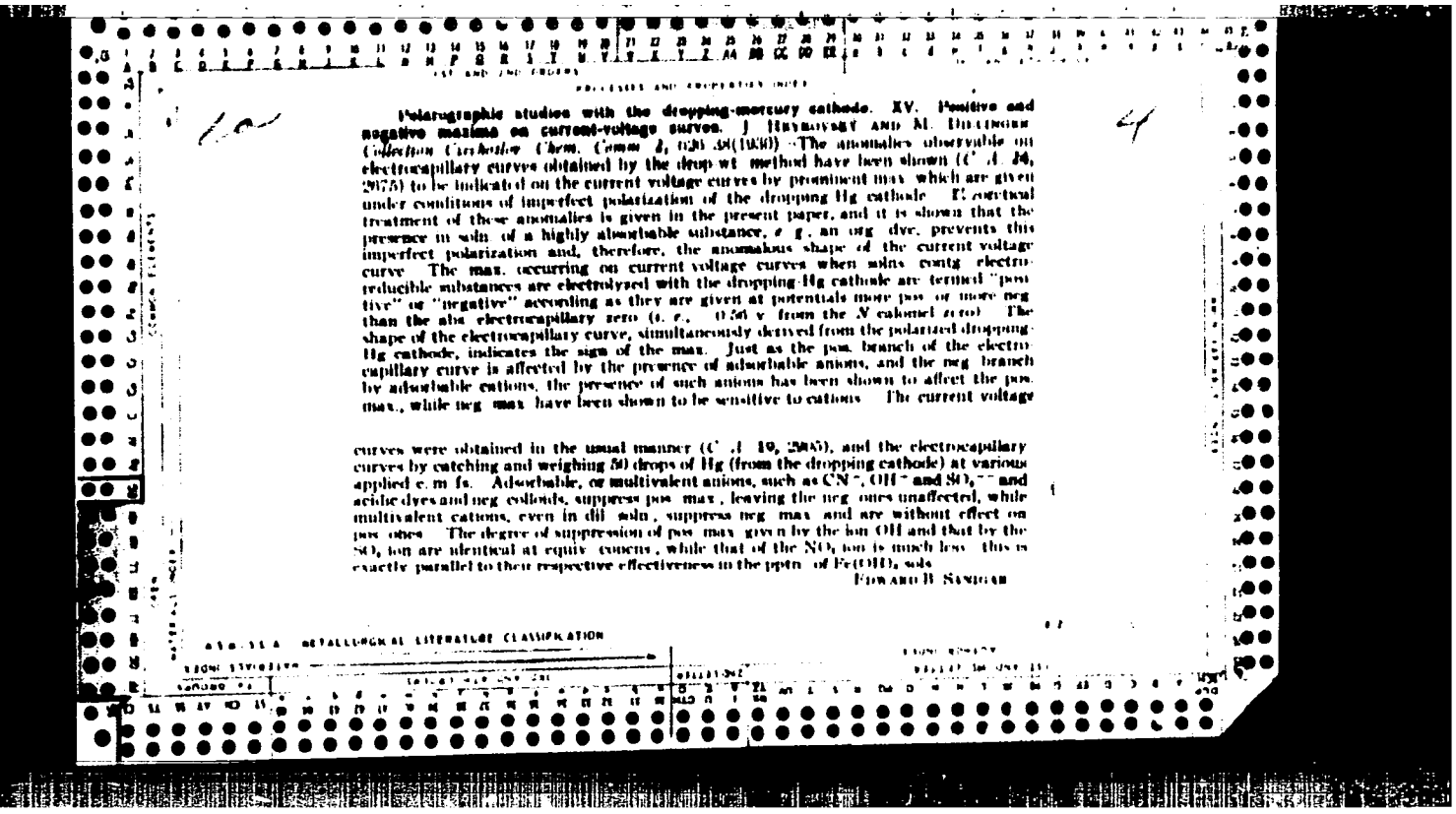
HEYROVSKY, Jaroslav 1890 -

Maxima on current-voltage curves. III. The electrolysis of mercury salt solutions with dropping and steady mercury cathods. P. Herasymenko and J. Heyrovsky and K. Tancakivsky. Trans. Faraday Soc. 25, 152-9 (1929)

HEYROVSKY, Jaroslav 1890 -

A study of some complexes by the polarigraphic method. M. N. Demassieux and J. Heyrovsky. Bull. soc. chim. 45, 30-5 (1929)



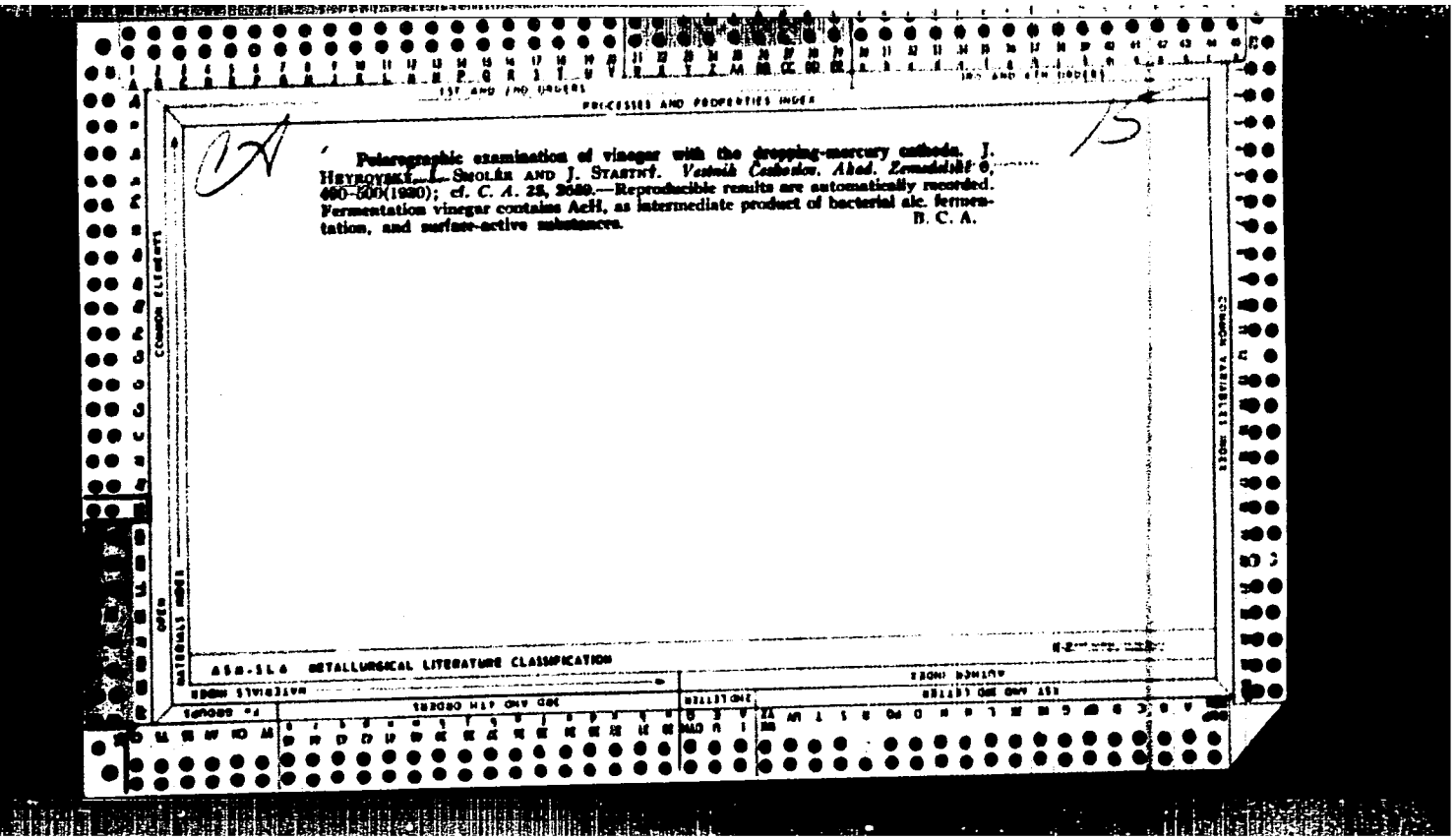


Polarographic studies with the dropping-mercury cathode. XV. Positive and negative maxima on current-voltage curves. J. Heyrovský and M. Dzierzgowski. *Collection Czechoslov. Chem. Comm.* 3, 620-38(1931).—The anomalies observable on electrocapillary curves obtained by the drop wt. method have been shown (C. A. 24, 2075) to be indicated on the current voltage curves by prominent max. which are given under conditions of imperfect polarization of the dropping Hg cathode. H. contrast treatment of these anomalies is given in the present paper, and it is shown that the presence in soln. of a highly absorbable substance, *e. g.*, an org. dye, prevents this imperfect polarization and, therefore, the anomalous shape of the current voltage curve. The max. occurring on current voltage curves when solns. contg. electroreducible substances are electrolyzed with the dropping-Hg cathode are termed "positive" or "negative" according as they are given at potentials more pos. or more neg. than the abs. electrocapillary zero (*e. g.*, −0.56 v. from the *N* calomel electr.). The shape of the electrocapillary curve, simultaneously derived from the polarized dropping-Hg cathode, indicates the sign of the max. Just as the pos. branch of the electrocapillary curve is affected by the presence of absorbable anions, and the neg. branch by absorbable cations, the presence of such anions has been shown to affect the pos. max., while neg. max. have been shown to be sensitive to cations. The current voltage curves were obtained in the usual manner (C. A. 19, 2885), and the electrocapillary curves by catching and weighing 50 drops of Hg (from the dropping cathode) at various applied e. m. fs. Absorbable, or multivalent anions, such as CN^-, OH^- and SO_4^{--}, and acidic dyes and neg. colloids, suppress pos. max., leaving the neg. ones unaffected, while multivalent cations, even in dil. soln., suppress neg. max. and are without effect on pos. ones. The degree of suppression of pos. max. given by the ion OH and that by the SO_4 ion are identical at equiv. concns., while that of the NO_3 ion is much less; this is exactly parallel to their respective effectiveness in the pptn. of $Fe(OH)_3$ sols.

Edward B. Sanigar

HEYROVSKY, Jaroslav 1890 -

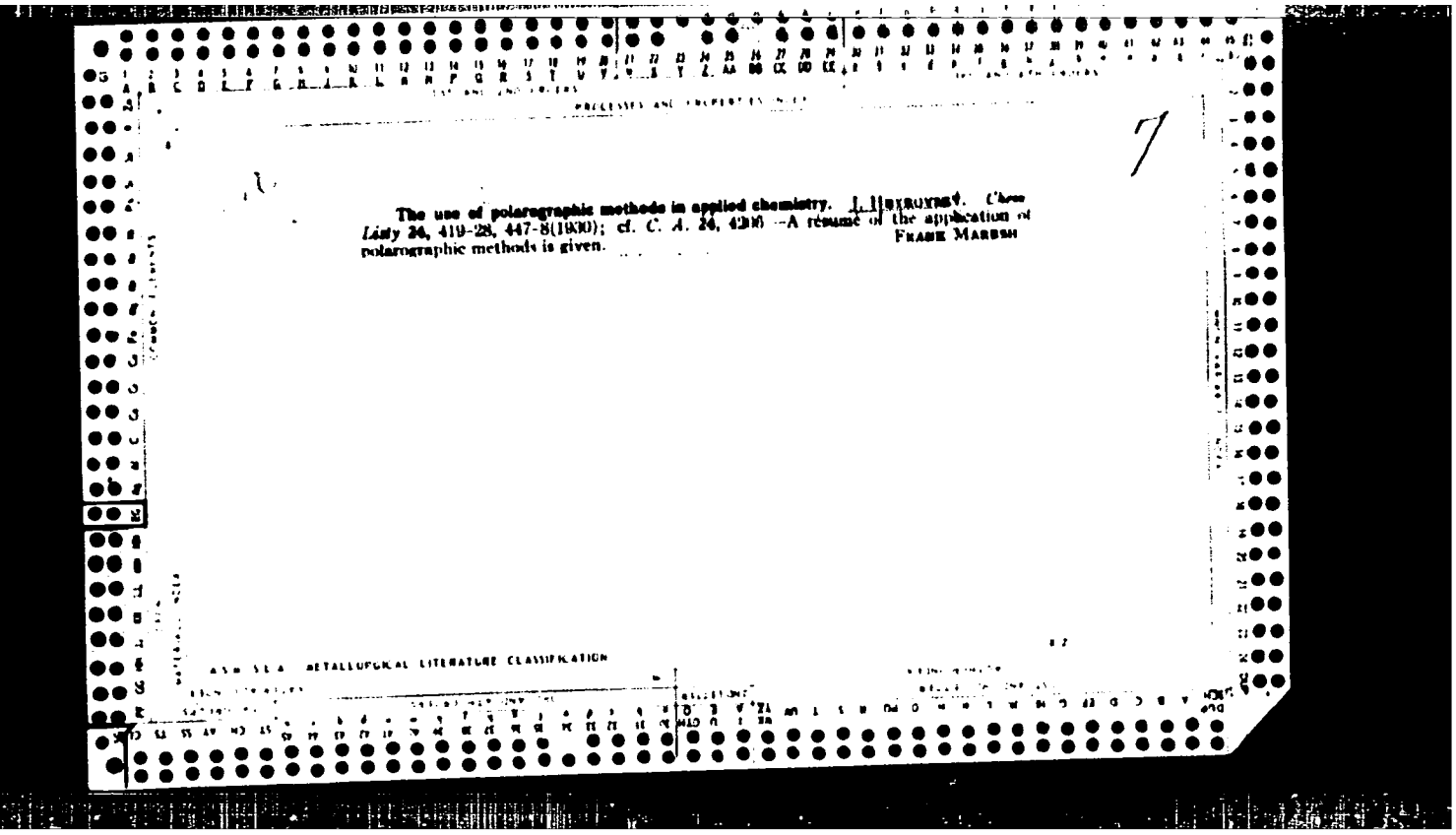
_____ and J. Babicka: P.S.D.M. Kathode. The effect of proteins. Chem. News 141, 369 and 385 (1930)



PROCESSES AND PROPERTIES INDEX

Polarographic examination of vinegar with the dropping-mercury cathode. J. Heyrovský, L. Sholár and J. Stastný. *Vestník Českého Akad. Zemědělské* 6, 480–500(1930); *cf. C. A.* 25, 2080.—Reproducible results are automatically recorded. Fermentation vinegar contains AcH, as intermediate product of bacterial alc. fermentation, and surface-active substances. B. C. A.

A58-SL6 METALLURGICAL LITERATURE CLASSIFICATION



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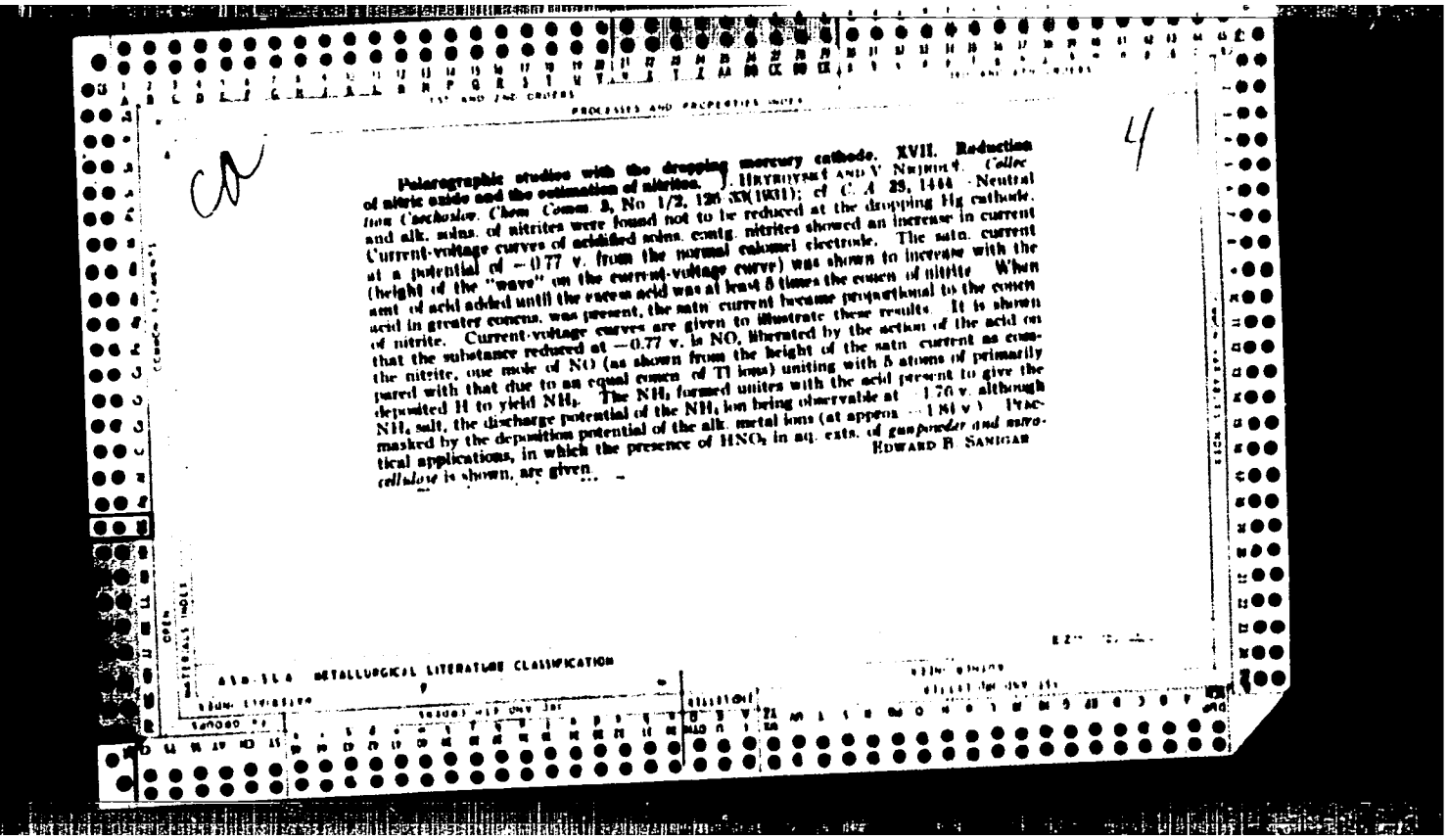
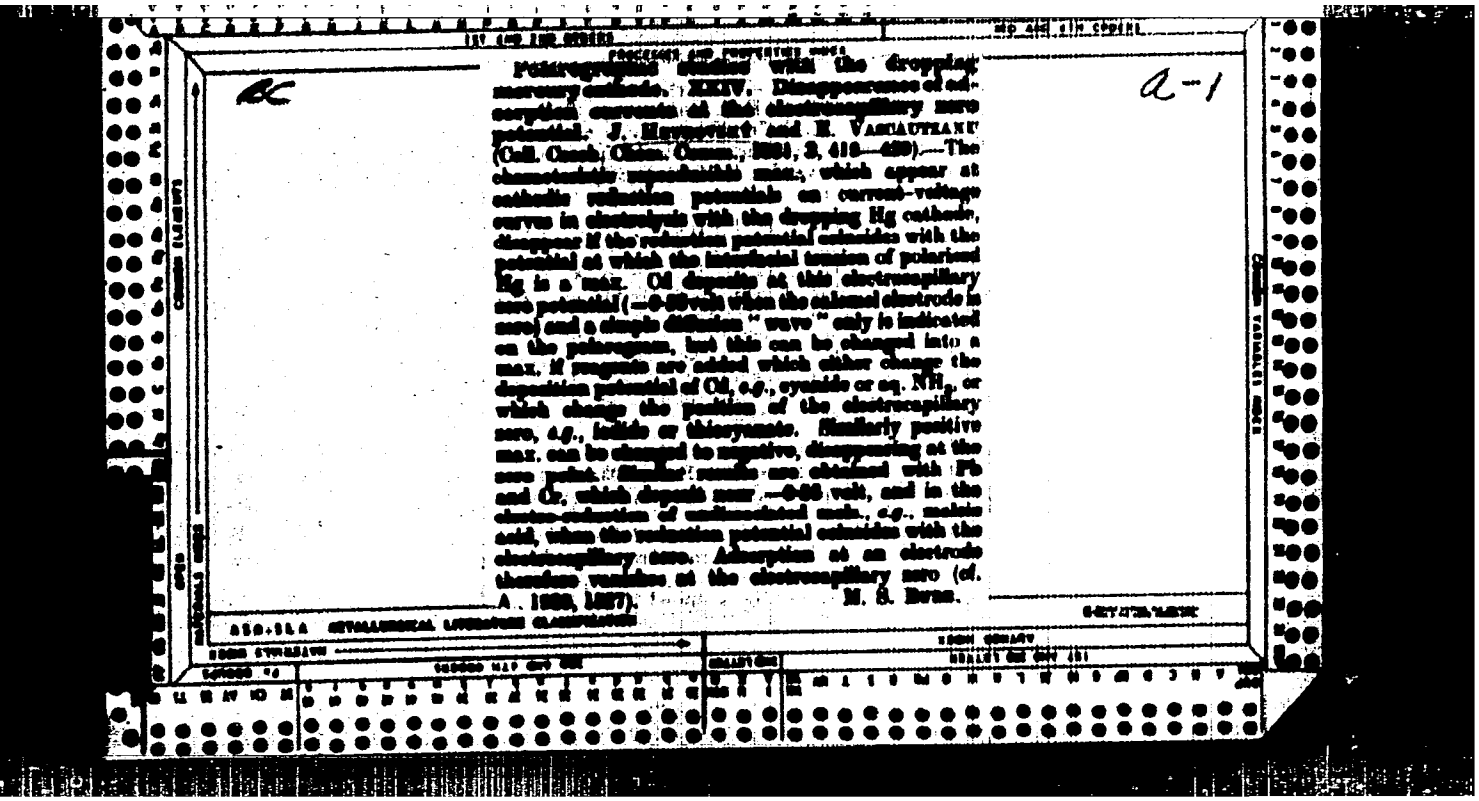
The use of polarographic methods in applied chemistry. J. [illegible]. Chem. *Listy* **24**, 419-28, 447-8(1930); cf. *C. A.* **24**, 4236.—A résumé of the application of polarographic methods is given.

FRANK MARSH



Polarographic studies with the dropping mercury cathode. XVII. Reduction of nitric oxide and the estimation of nitrites. J. HEYROVSKÝ AND V. NEJEDLÝ. *Collection Czechoslov. Chem. Comm.* **3**, No. 1/2, 120–33(1931); cf. *C. A.* **25**, 1444. Neutral and alk. solns. of nitrites were found not to be reduced at the dropping Hg cathode. Current-voltage curves of acidified solns. contg. nitrites showed an increase in current at a potential of −0.77 v. (from the normal calomel electrode). The satn. current (height of the "wave" on the current-voltage curve) was shown to increase with the amt. of acid added until the excess acid was at least 5 times the concn. of nitrite. When acid in greater concns. was present, the satn. current became proportional to the concn. of nitrite. Current-voltage curves are given to illustrate these results. It is shown that the substance reduced at −0.77 v. is NO, liberated by the action of the acid on the nitrite, one mole of NO (as shown from the height of the satn. current as compared with that due to an equal concn. of Tl ions) uniting with 5 atoms of primarily deposited H to yield NH_3. The NH_3 formed unites with the acid present to give the NH_4 salt, the discharge potential of the NH_4 ion being observable at −1.76 v. although masked by the deposition potential of the alk. metal ions (at approx. −1.81 v.). Practical applications, in which the presence of HNO_3 in aq. exts. of *gunpowder* and *nitrocellulose* is shown, are given. EDWARD B. SANIGAR



Polarographic studies with the dropping mercury cathode. XXIV. Disappearance of adsorption currents at the electrocapillary zero potential. J. Heyrovský and R. Vasiautrany (Coll. Czech. Chem. Comm., 1931, 3, 413—429).—The characteristic unpolarisable min., which appear at cathodic reduction potentials on current-voltage curves in electrolysis with the dropping Hg cathode, disappear if the reduction potential coincides with the potential at which the interfacial tension of polarised Hg is a max. Cd deposits at this electrocapillary zero potential (−0·52 volt when the calomel electrode is zero) and a simple diffusion "wave" only is indicated on the polarogram, but this can be changed into a max. if reagents are added which either change the deposition potential of Cd, e.g., cyanide or aq. NH_3, or which change the position of the electrocapillary zero, e.g., iodide or thiocyanate. Similarly positive max. can be changed to negative, disappearing at the zero point. Similar results are obtained with Pb and Cr, which deposit near −0·65 volt, and in the electro-reduction of unsaturated acids, e.g., maleic acid, when the reduction potential coincides with the electrocapillary zero. Adsorption at an electrode therefore vanishes at the electrocapillary zero (cf. A., 1929, 1257).

M. S. Burr.

Estimation of oxygen by the polarographic method. J. HEYROVSKÝ. *Trav. Trav.* 5, 162-71(171-3 English)(1931).—Current-voltage curves obtained in electrolysis with the dropping Hg cathode and a large Hg anode are strictly reproducible and permit qual. as well as quant. conclusions on electro-reducible substances present in the electrolyzed soln. The method is very convenient if automatic recording of current-voltage curves is made photographically by a polarograph. The curves obtained from solns. electrolyzed when exposed to air always show two summits (two "waves") which are due to the reduction of O to H_2O_2 and then to H_2O. When 0.3% H_2O_2 is dropped into 20 cc. 0.1 *M* salicylic acid an increase in the 2nd wave can be seen. In this way H_2O_2 and all peroxides can be detd. In alk. solns., however, H_2O_2 is unstable, decomps. to O. Curves are given for various expts. One curve serves as an example of quant. estn. of O in tech. gases. The sensitivity of the method is such that 0.2% O in gases or 0.1 ml. per l. of soln. may be estd. with 5% accuracy, 1 cc. of the soln. being sufficient for analysis and the curve being obtained in 5 min. In one figure a decrease of O is shown by curves to the solns. in which plants are decaying. The method is reliable only in the absence of oxidizing agents and ions of nobler metals, which may be easily removed by alkali hydroxides.

J. KUČERA

HEYROVSKY, Jaroslav 1890 -

Analysis of petroleum and its distillates for reducible substances and the adsorbable matter by means of the polarographic method with the dropping-mercury cathode. B. Gosman and J. Heyrovsky. Trans Electrochem. Soc. 59 (preprint), 23 pp. (1931) - pp. 249-271

Also appears in J. Amer. Electrochem. Soc. 27, IV (1931)

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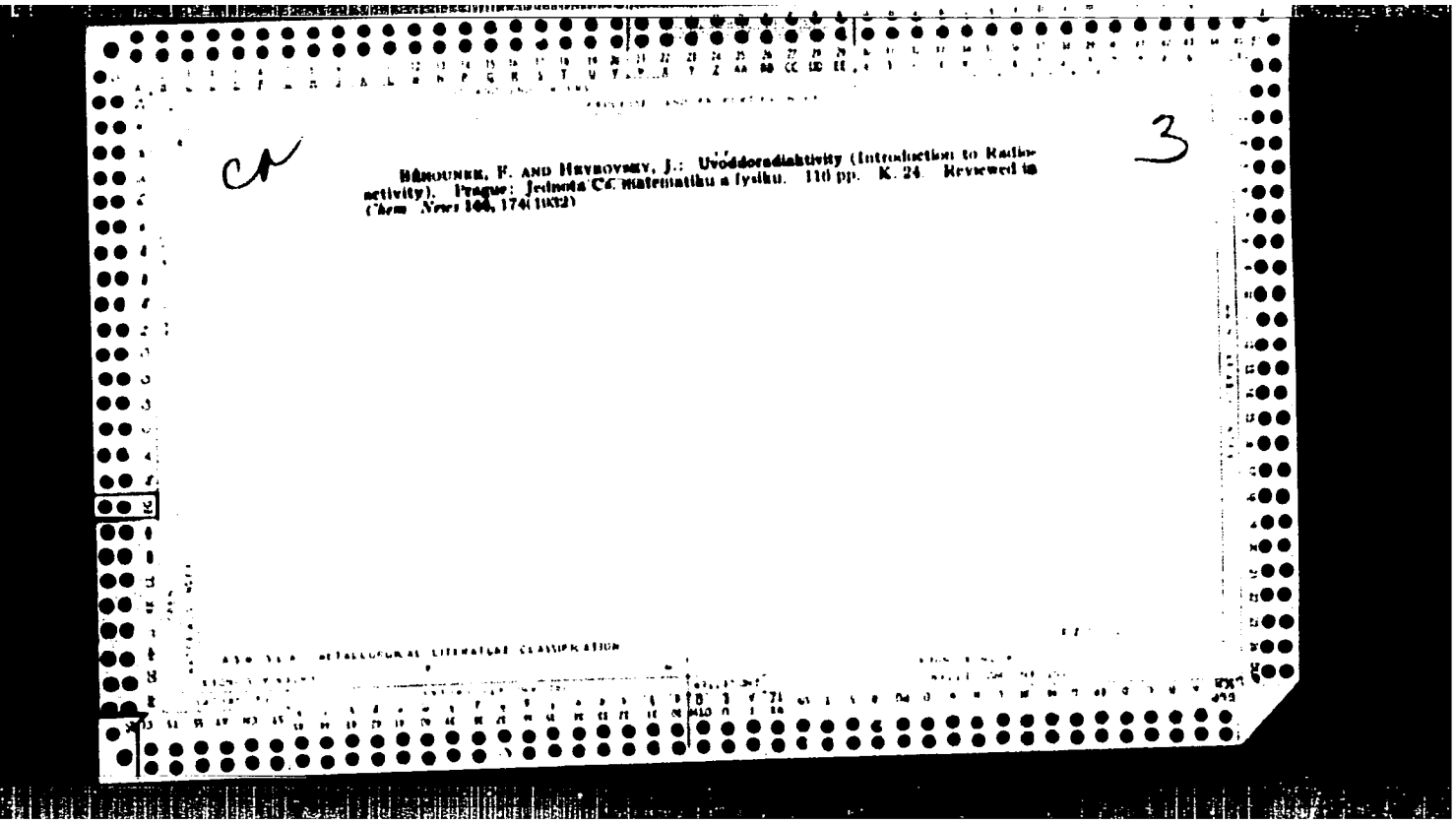
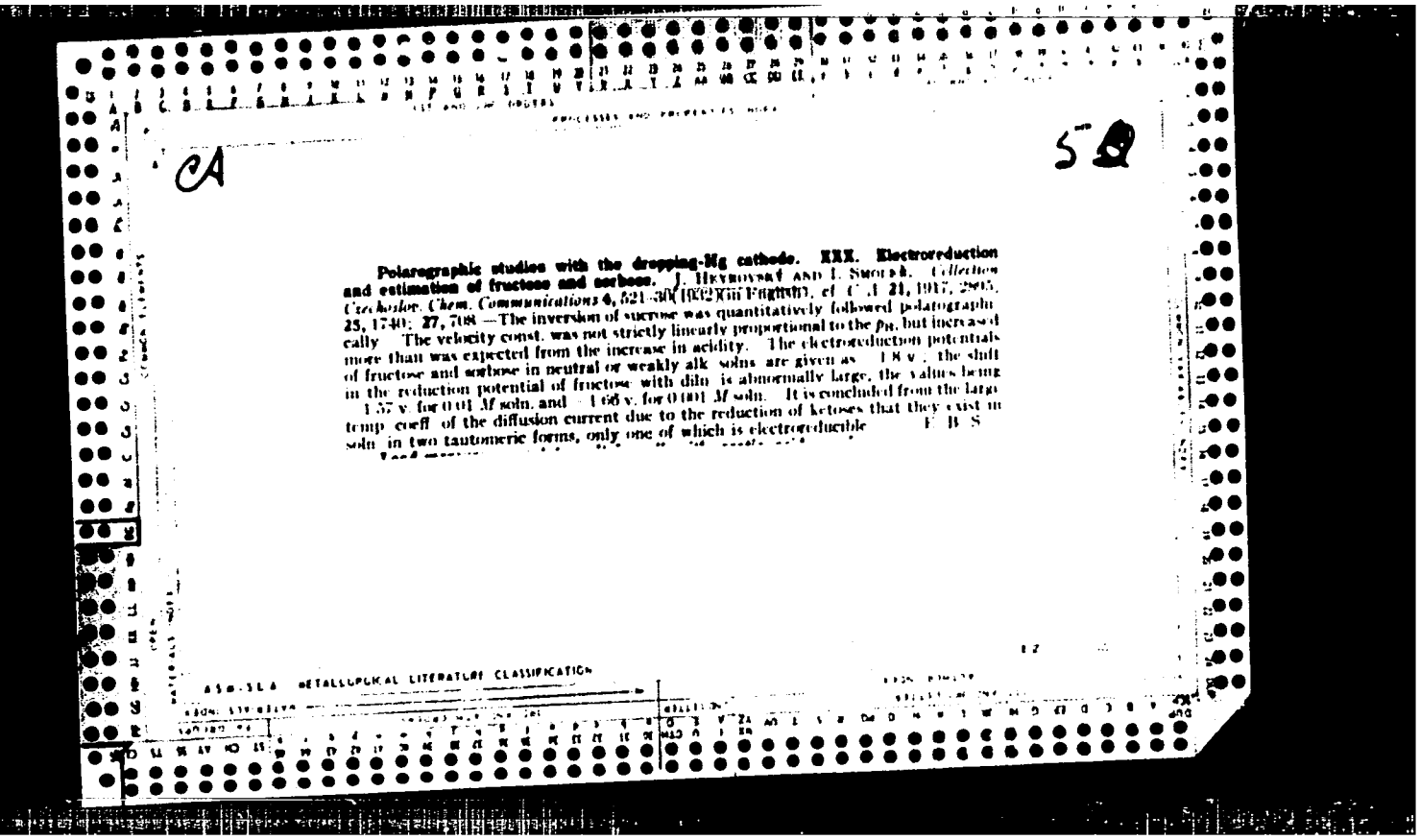
_____and V. Nejedly. The electroreduction of nitric oxide and the estimation of nitrites at the dropping mercury cathode. Chem. News 142, 193-97 (1931)



BÁRDUNEK, F. AND HAVRDOVSKÝ, J.: Uvoddoradiaktivity (Introduction to Radioactivity). Prague: Jednota Čs. matematiku a fysiku. 110 pp. K. 24. Reviewed in (Chem. News 146, 174 (1932)



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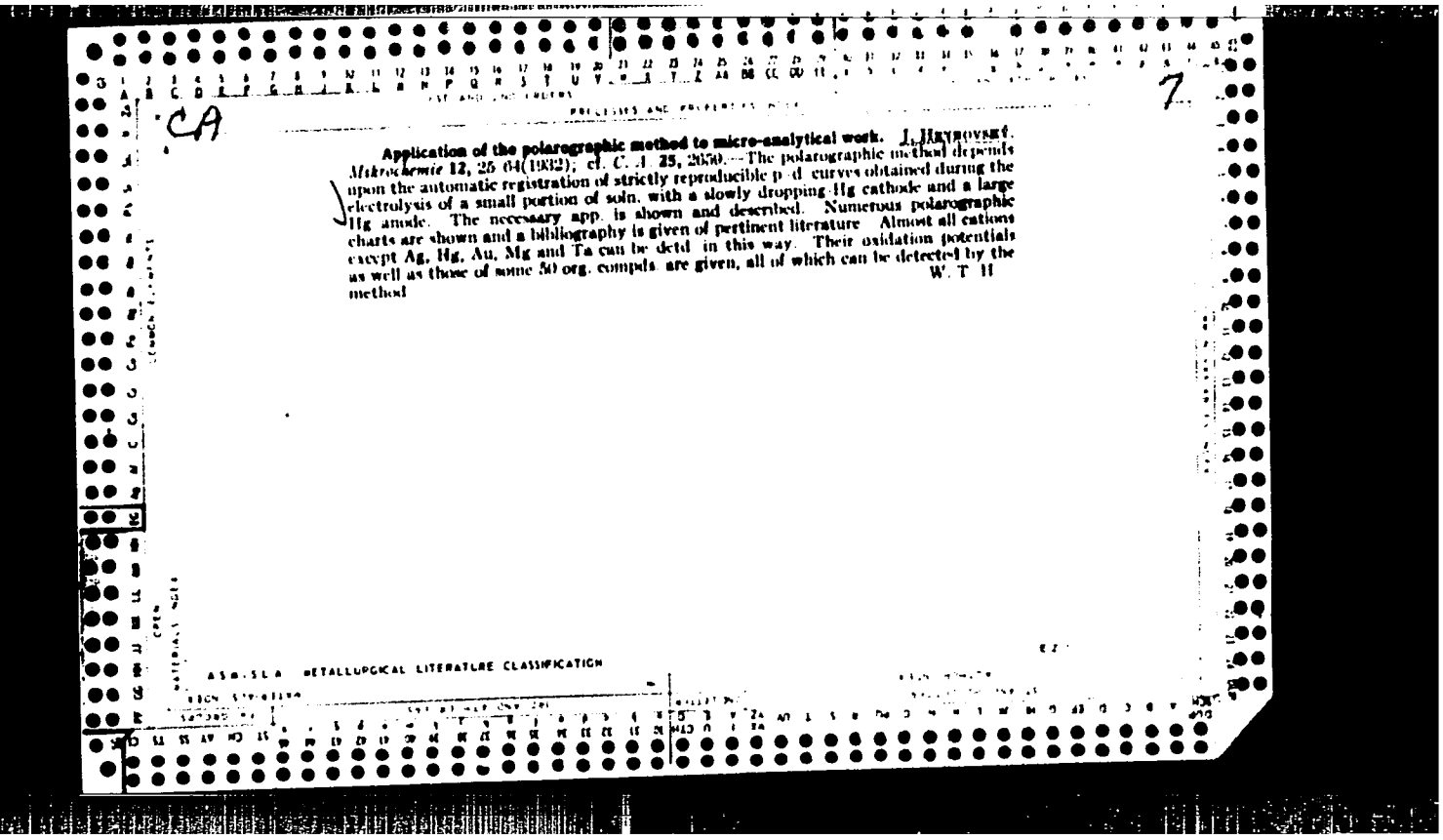
Polarographic studies with the dropping-Hg cathode. XXX. Electroreduction and estimation of fructose and sorbose. J. Heyrovský and I. Smoler. *Collection Czechoslov. Chem. Communications* 6, 521–30 (1934) (in English). cf. *C. A.* 21, 1917, 2905; 25, 1740; 27, 708.—The inversion of sucrose was quantitatively followed polarographically. The velocity const. was not strictly linearly proportional to the p_H but increased more than was expected from the increase in acidity. The electroreduction potentials of fructose and sorbose in neutral or weakly alk. solns are given as −1.8 v.; the shift in the reduction potential of fructose with dilu. is abnormally large, the values being −1.57 v. for 0.01 *M* soln. and −1.66 v. for 0.001 *M* soln. It is concluded from the large temp. coeff. of the diffusion current due to the reduction of ketoses that they exist in soln. in two tautomeric forms, only one of which is electroreducible. F. B. S.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



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Application of the polarographic method to micro-analytical work. J. Heyrovský. *Mikrochemie* **12**, 25-64(1932); cf. *C. A.* **25**, 2050.—The polarographic method depends upon the automatic registration of strictly reproducible p-d curves obtained during the electrolysis of a small portion of soln. with a slowly dropping Hg cathode and a large Hg anode. The necessary app. is shown and described. Numerous polarographic charts are shown and a bibliography is given of pertinent literature. Almost all cations except Ag, Hg, Au, Mg and Ta can be detd. in this way. Their oxidation potentials as well as those of some 50 org. compds. are given, all of which can be detected by the method. W. T. H

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Der Polarograph und seine Anwendung (tschech., 4 S.
Elektrotechnicky obzor 21, 37 (1932).

1ST AND 2ND ORDERS

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The reduction of fructose by the mercury drop cathode and the determination of invertose by the polarographic method. J. Heyrovský and I. Smoler. *Chem. Listy* 26, 479-84(1932).—The ketoses fructose and sorbose were reduced by the Hg drop cathode in neutral or slightly alk. solns. at a potential of —1.80 v. The polarographic curve shows a rise in the current which is directly proportional to the concn. of the ketose. The aldoses glucose, mannose, rhamnose, *l*-arabinose and lyxose and the bioses sucrose, maltose and lactose are not reduced by the cathode; their presence has no influence upon the course of the reduction of ketoses. Fructose and invertose were detd. in solns. of sucrose and honey with a precision of 2-10% in concns. of 0.001% of the ketoses; 0.2 cc. of soln. sufficed for the detn. The easier reduction of the ketose rather than the aldose is ascribed to the presence of the large no. of acidic OH groups which influences the fundamental constitution and makes the ketose susceptible to electroreduction. Because of temp. changes during the reduction, abnormal deviations occur in the polarographic curve; definite conclusions about the current required for a g. mol. of the reducing substance are not possible. Frank Maresh

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Anwendung der polarographischen Methode in der praktischen Chemie (tschech.). Prag: Institut der "Akademie der Arbeit", 1935

PROCESSES AND PROPERTIES INDEX

Polarographic examination of fermentation products. J. Heyrovský, J. Smoler and J. Šťastný. *Věstník Českoslov. Akad. Zemědělské* 9, 589-607(1933); *Chem. Obzor* 9, Abstract sect., 220.—Fructose could be detd. in wine more easily by the polarographic than by the polarimetric method in the presence of other optically active substances. The presence of fructose does not prevent the detn. of proteins. Of the acids only malic acid could be detd. with some accuracy. Synthetic EtOH can be distinguished from that produced by fermentation. An aliphatic aldehyde was found in the synthetic alc. which is not present in fermentation alc. The polarographic method gives valuable results in the analysis of alcs. contg. traces of heavy metals such as Cu and Zn.

J. Kučera

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Anwendung der polarographischen Methode in der praktischen Chemie (tscheck.). Verlag Csl. svaz pro vyzkum a zkouseni technicky dulezitych latek a konstrukci. Ustav Masarykovy akademie Prace (1933), No. 10, 124 S.

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Industrial applications of the polarographic method of analysis.
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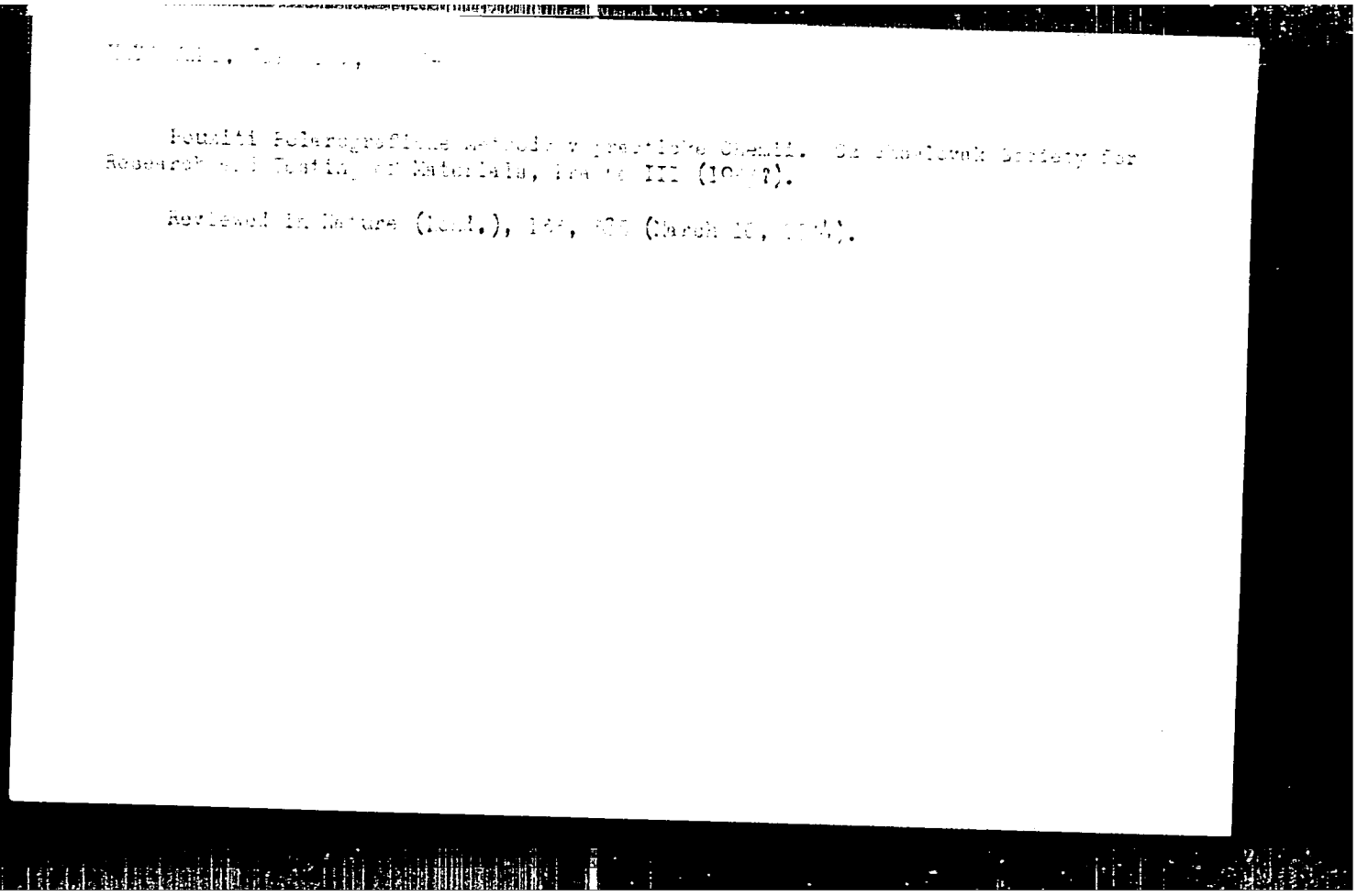
(Note: Another index lists this as Chimie & industrie, 29, No 6 bis, 204-211 (1933)



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Reviewed in Nature (Lond.), 169, 457 (March 15, 1952).

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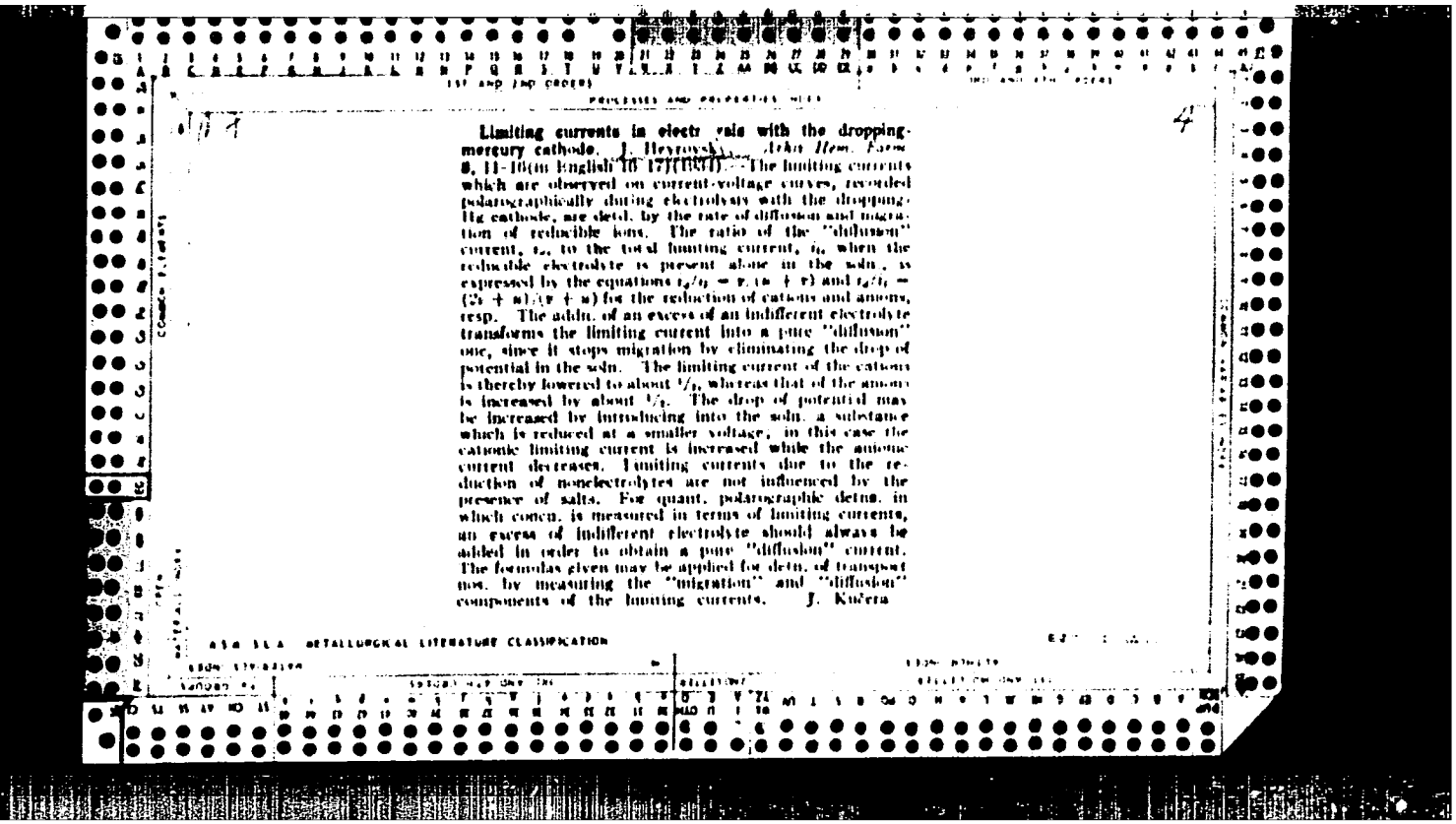
Die Theorie der Wasserstoffueberspannung und ihrer katalytischen Herabsetzung an der tropfenden Quecksilverelektrode (russ.). Trudy jubileinogo Mendeleevskogo sjezda 1934, 305-309.

The theory of overpotential of hydrogen and its catalytic lowering at the dropping mercury cathode. Travaux du congres jubilaire Mendeleev, p. 299-303. Moscou, Leningrad: Edition de l'Academie des sciences de l'URSS, 1937.

HEYROVSKY, Jaroslav 1890 -

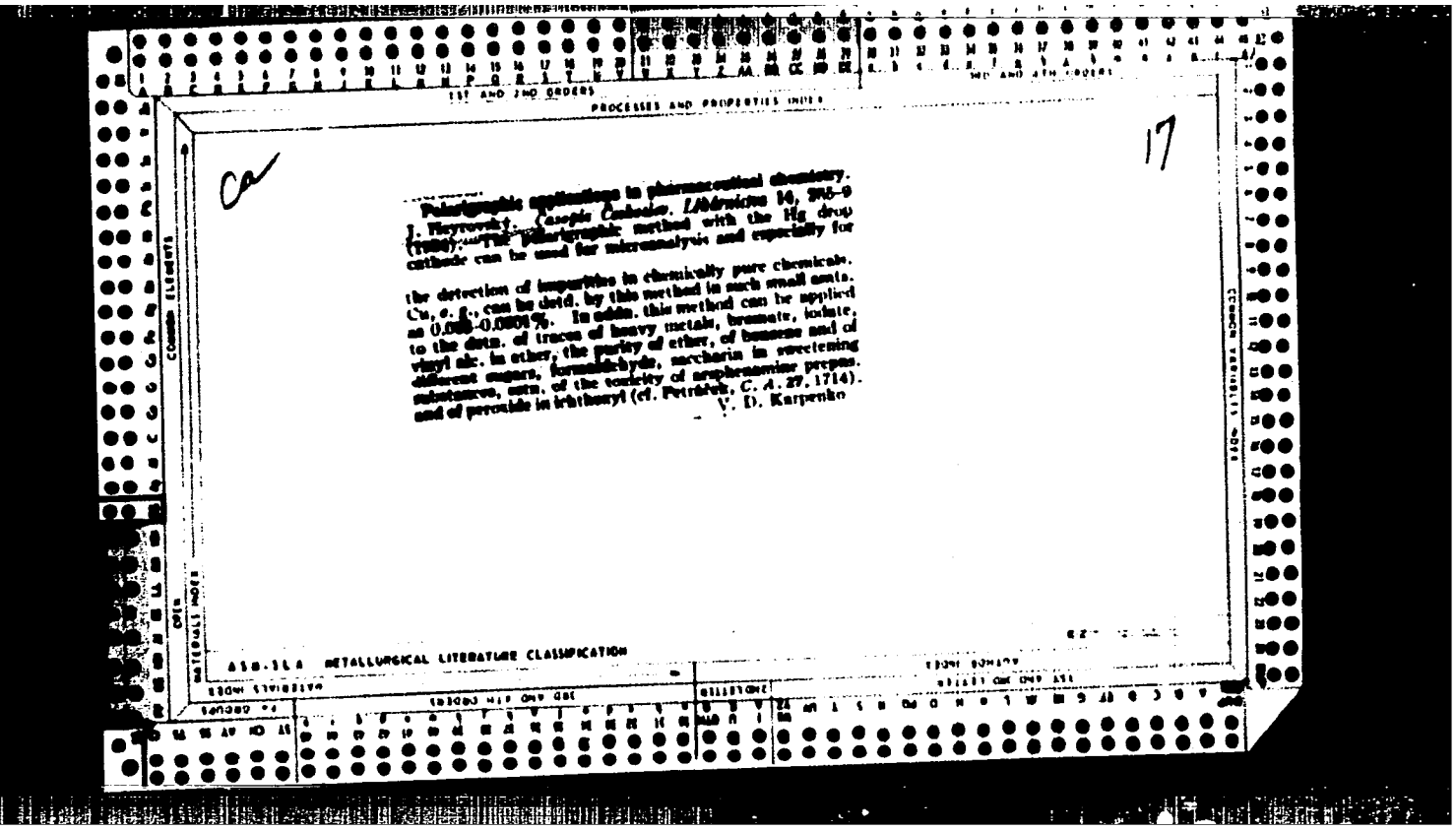
A polarographic study of the electro-kinetic phenomena of adsorption, electro-reduction and overpotential displayed at the dropping mercury cathod. Paris, Hermann et cie, 1934. Bibliog, p. 47-8
Actualites scientifiques et industrielles No 90.



Limiting currents in electr ysis with the dropping-mercury cathode. J. Heyrovský. *Archiv Hem. Farm.* 5, 11-16(in English 16-17)(1931).—The limiting currents which are observed on current-voltage curves, recorded polarographically during electrolysis with the dropping-Hg cathode, are detd. by the rate of diffusion and migration of reducible ions. The ratio of the "diffusion" current, i_d, to the total limiting current, i_l, when the reducible electrolyte is present alone in the soln., is expressed by the equations $i_d/i_l = v/(u + v)$ and $i_d/i_l = (2v + u)/(v + u)$ for the reduction of cations and anions, resp. The addn. of an excess of an indifferent electrolyte transforms the limiting current into a pure "diffusion" one, since it stops migration by eliminating the drop of potential in the soln. The limiting current of the cations is thereby lowered to about $^1/_2$, whereas that of the anions is increased by about $^1/_2$. The drop of potential may be increased by introducing into the soln. a substance which is reduced at a smaller voltage, in this case the cationic limiting current is increased while the anionic current decreases. Limiting currents due to the reduction of nonelectrolytes are not influenced by the presence of salts. For quant. polarographic detns. in which concn. is measured in terms of limiting currents, an excess of indifferent electrolyte should always be added in order to obtain a pure "diffusion" current. The formulas given may be applied for detn. of transport nos. by measuring the "migration" and "diffusion" components of the limiting currents. J. Kučera

HEYROVSKY, Jaroslav 1890 -

Polarographische Untersuchungen von Mineralwaessern (tschech.). Vestnik balneol. a klimatol. spol. 14, 88-94 (1934)



Polarographic applications in pharmaceutical chemistry. J. Heyrovský. *Casopis Československ. Lékárnictva* 14, 305-9 (1934). The polarographic method with the Hg drop cathode can be used for microanalysis and especially for

the detection of impurities in chemically pure chemicals. Cu, e. g., can be detd. by this method in such small amts. as 0.005-0.0001%. In addn. this method can be applied to the detn. of traces of heavy metals, bromate, iodate, vinyl alc. in ether, the purity of ether, of benzene and of different sugars, formaldehyde, saccharin in sweetening substances, extn. of the toxicity of neoarsenamine prepns. and of peroxide in erythrityl (cf. Petrášek, *C. A.* 27, 1714).

V. D. Karpenko

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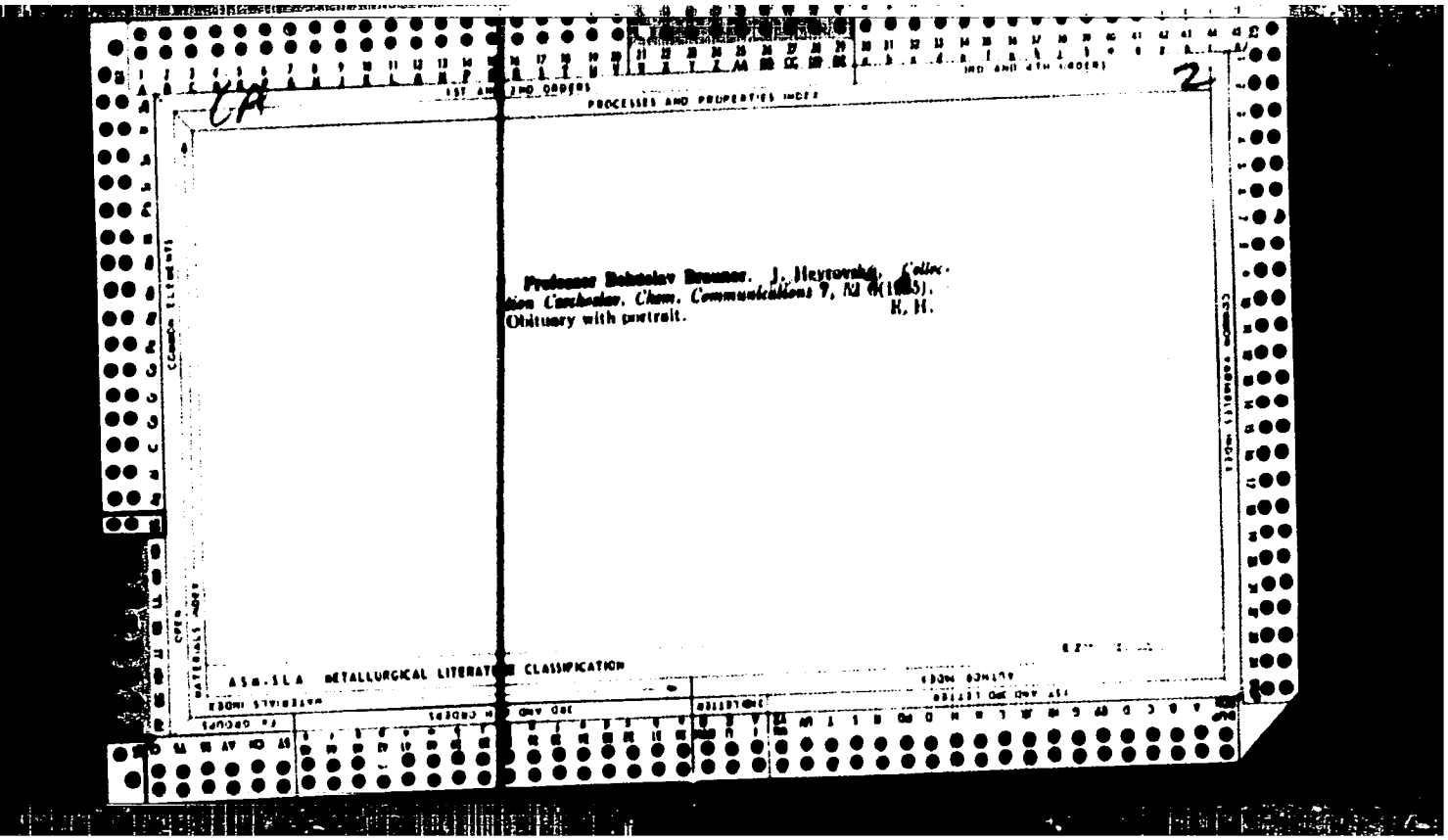
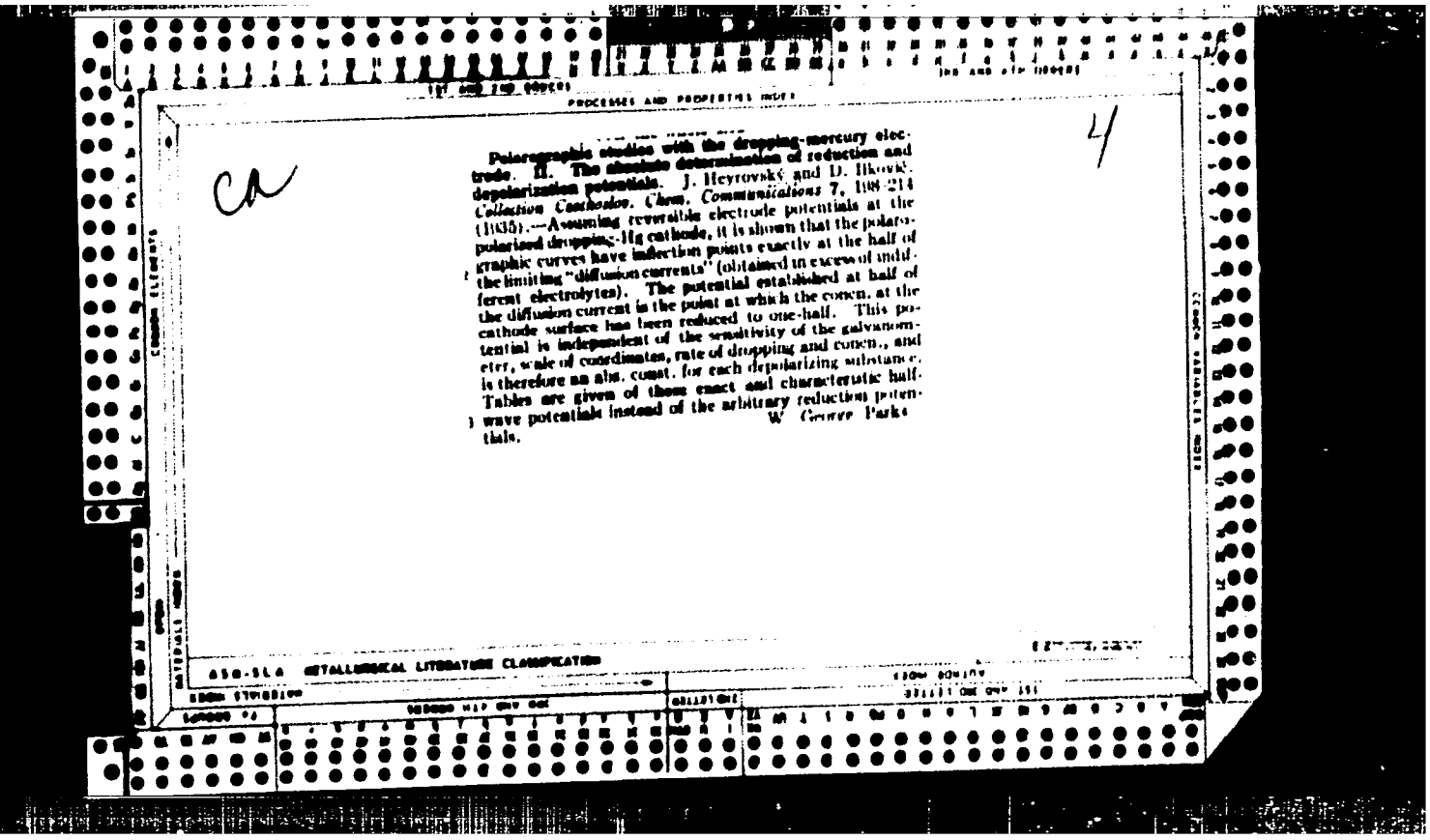
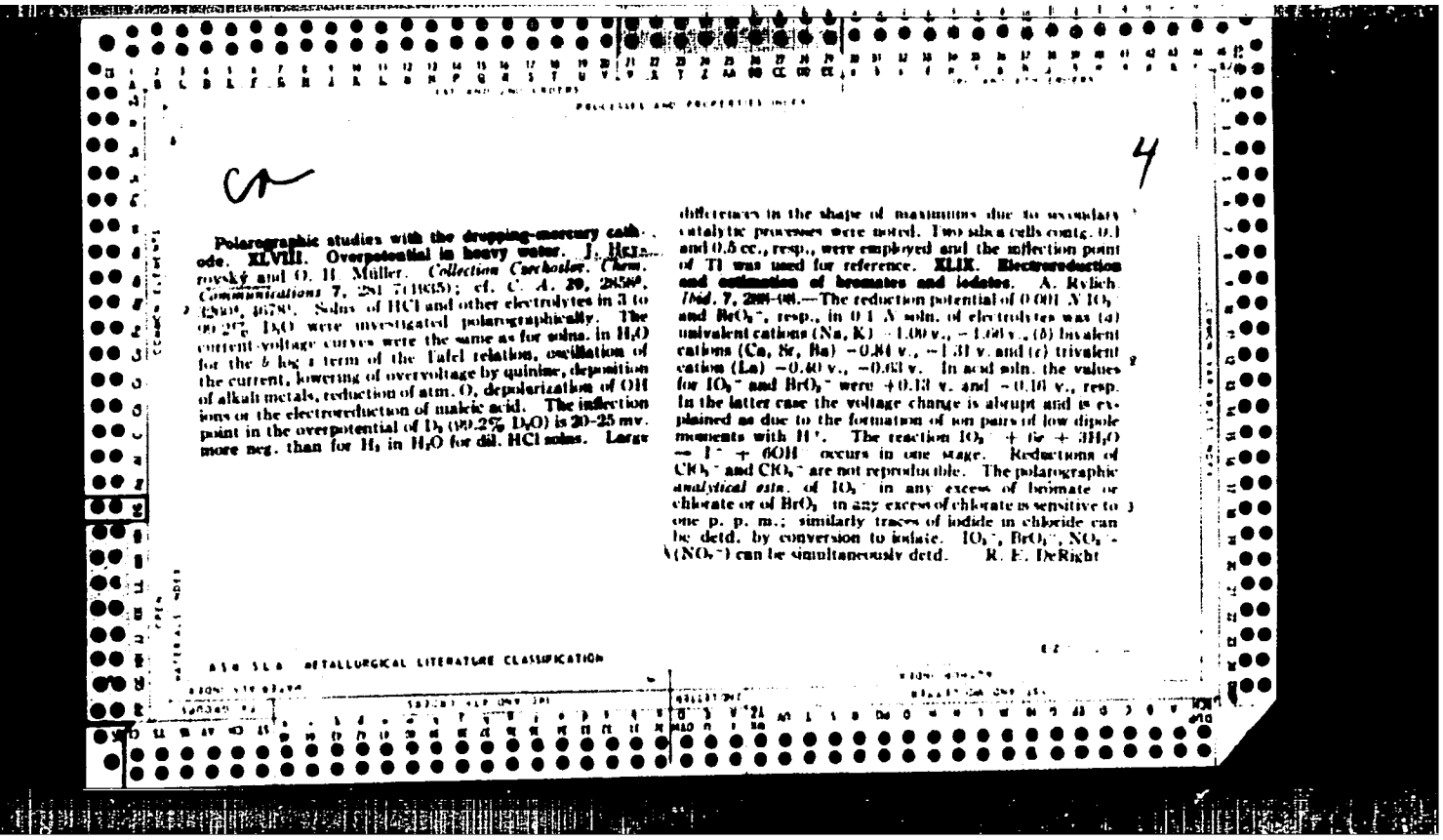
A58-31A METALLURGICAL LITERATURE CLASSIFICATION





Polarographic studies with the dropping-mercury electrode. II. The absolute determination of reduction and depolarization potentials. J. Heyrovský and D. Ilkovič. *Collection Czechoslov. Chem. Communications* 7, 198-214 (1935).—Assuming reversible electrode potentials at the polarized dropping-Hg cathode, it is shown that the polarographic curves have inflection points exactly at the half of the limiting "diffusion currents" (obtained in excess of indifferent electrolytes). The potential established at half of the diffusion current is the point at which the concn. at the cathode surface has been reduced to one-half. This potential is independent of the sensitivity of the galvanometer, scale of coordinates, rate of dropping and concn., and is therefore an abs. const. for each depolarizing substance. Tables are given of these exact and characteristic half-wave potentials instead of the arbitrary reduction potentials.

W. Conwy Parks



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Polarographic studies with the dropping-mercury cathode. XLVIII. Overpotential in heavy water. J. Heyrovský and O. H. Müller. *Collection Czechoslov. Chem. Communications* 7, 281–7(1935); cf. *C. A.* **29**, 2858⁹, 6930, 6978. Solns. of HCl and other electrolytes in 3 to 99.2% D_2O were investigated polarographically. The current-voltage curves were the same as for solns. in H_2O for the $b \log i$ term of the Tafel relation, oscillation of the current, lowering of overvoltage by quinine, deposition of alkali metals, reduction of atm. O, depolarization of OH ions on the electroreduction of malonic acid. The inflection point in the overpotential of D_2 (99.2% D_2O) is 20–25 mv. more neg. than for H_2 in H_2O for dil. HCl solns. Large differences in the shape of maximums due to secondary catalytic processes were noted. Two silica cells contg. 0.1 and 0.5 cc., resp., were employed and the inflection point of Tl was used for reference. **XLIX. Electroreduction and estimation of bromates and iodates.** A. Rylich. *Ibid.* 7, 288–98.—The reduction potential of 0.001 *N* IO_3^- and BrO_3^-, resp., in 0.1 *N* soln. of electrolytes was (*a*) univalent cations (Na, K) −1.00 v., −1.66 v., (*b*) bivalent cations (Ca, Sr, Ba) −0.84 v., −1.31 v. and (*c*) trivalent cation (La) −0.40 v., −0.61 v. In acid soln. the values for IO_3^- and BrO_3^- were +0.13 v. and −0.16 v., resp. In the latter case the voltage change is abrupt and is explained as due to the formation of ion pairs of low dipole moments with H^+. The reaction $IO_3^- + 6e + 3H_2O \rightarrow I^- + 6OH^-$ occurs in one stage. Reductions of ClO_3^- and ClO_4^- are not reproducible. The polarographic *analytical soln.* of IO_3^- in any excess of bromate or chlorate or of BrO_3^- in any excess of chlorate is sensitive to one p. p. m.; similarly traces of iodide in chloride can be detd. by conversion to iodate. IO_3^-, BrO_3^-, NO_3^- (NO_2^-) can be simultaneously detd. R. E. DeRight

A 1 0 S L A METALLURGICAL LITERATURE CLASSIFICATION

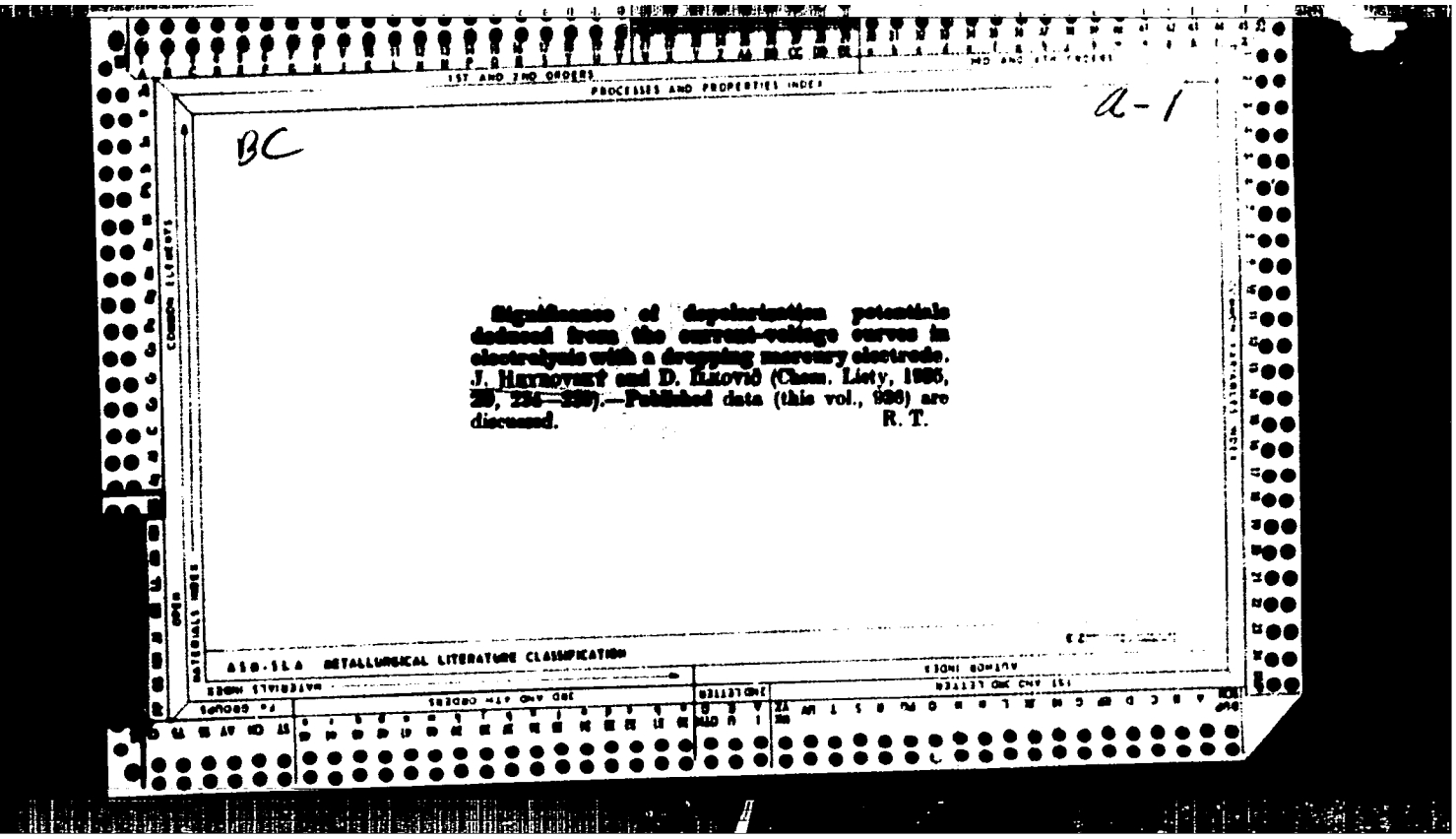
1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

4

The catalytic deposition of hydrogen on the dropping mercury cathode. —J. Heyrovský. *Příroda* 28, 212 ?0 (1935); *Chem. Obzor* 12, *Abstracts* 105.—Before the decompn. potentials were reached, curves for the salts of Ru, Rh, Ir and Pd had a wavelike appearance. The height of the waves was proportional to the acidity of the soln. and to the salt concn. Metals which readily dissolve in Hg (Au, Ag, Cu, Pb) did not show this effect. H. studied the effect of quinoline alkaloids and of the SH group of amino acids. Re sulfide pptd. from a neutral perrhenate soln. gave the most sensitive tests for Re in the Re salts. Frank Maresh

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



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Significance of depolarization potentials deduced from the current-voltage curves in electrolysis with a dropping mercury electrode. J. Heyrovský and D. Ilkovič (Chem. Listy, 1935, 29, 236—239).—Published data (this vol., 936) are discussed. R. T.

HEYROVSKY, Jaroslav 1890 -

Ueberspannung des schweren Wasserstoffes an der tropfenden Quecksilverelektrode (tschech., R.). Chem. Listy Vedu Prumysl 29, 295-300 (1935)

HEYROVSKY, Jaroslav 1890 -

A sensitive polarographic test for the absence of rhenium in manganous salts. Nature 135, 870-1 (1935) and [illegible] Nature, 137, 121 (1936)

also

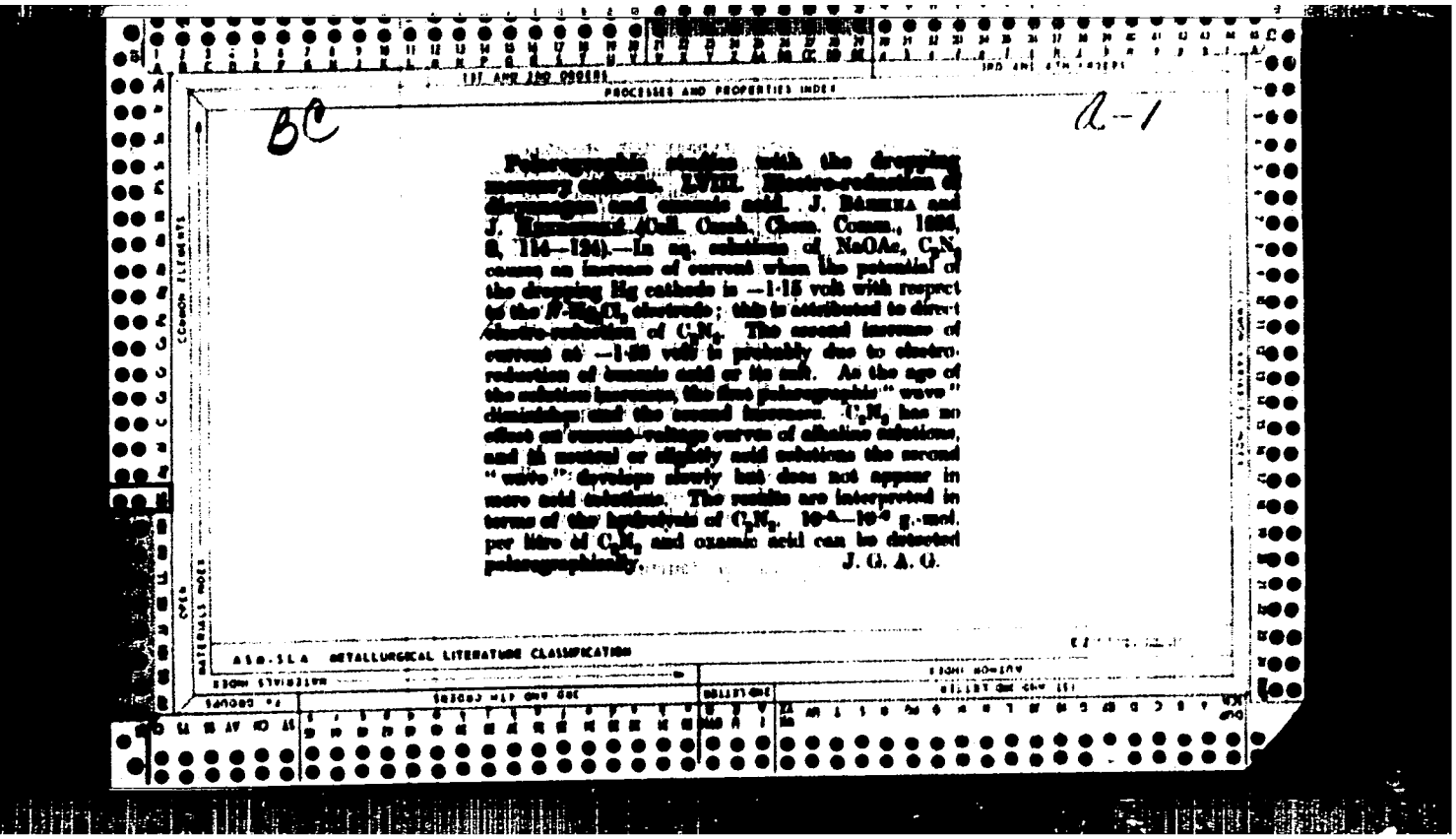
Ein empfindlicher polarographischer Nachweis der Abwesenheit des Rheniums in Mangansalzen (tschech., R.). 5 S. Rozpravy II tr. Ces. Akademie 45, No. 8 (1935) item Bull. int. Acad. Boheme 1935.

HEYROVSKY, Jaroslav [illegible] -

Polarographie, in W. Boettger: "Physikalische Methoden der analytischen Chemie", part 2, 260-322. Leipzig: Akademische Verlagsgesellschaft, 1936.

and

Fortschritte der Polarographie, in same reference, part 3, 422-77 (1939)



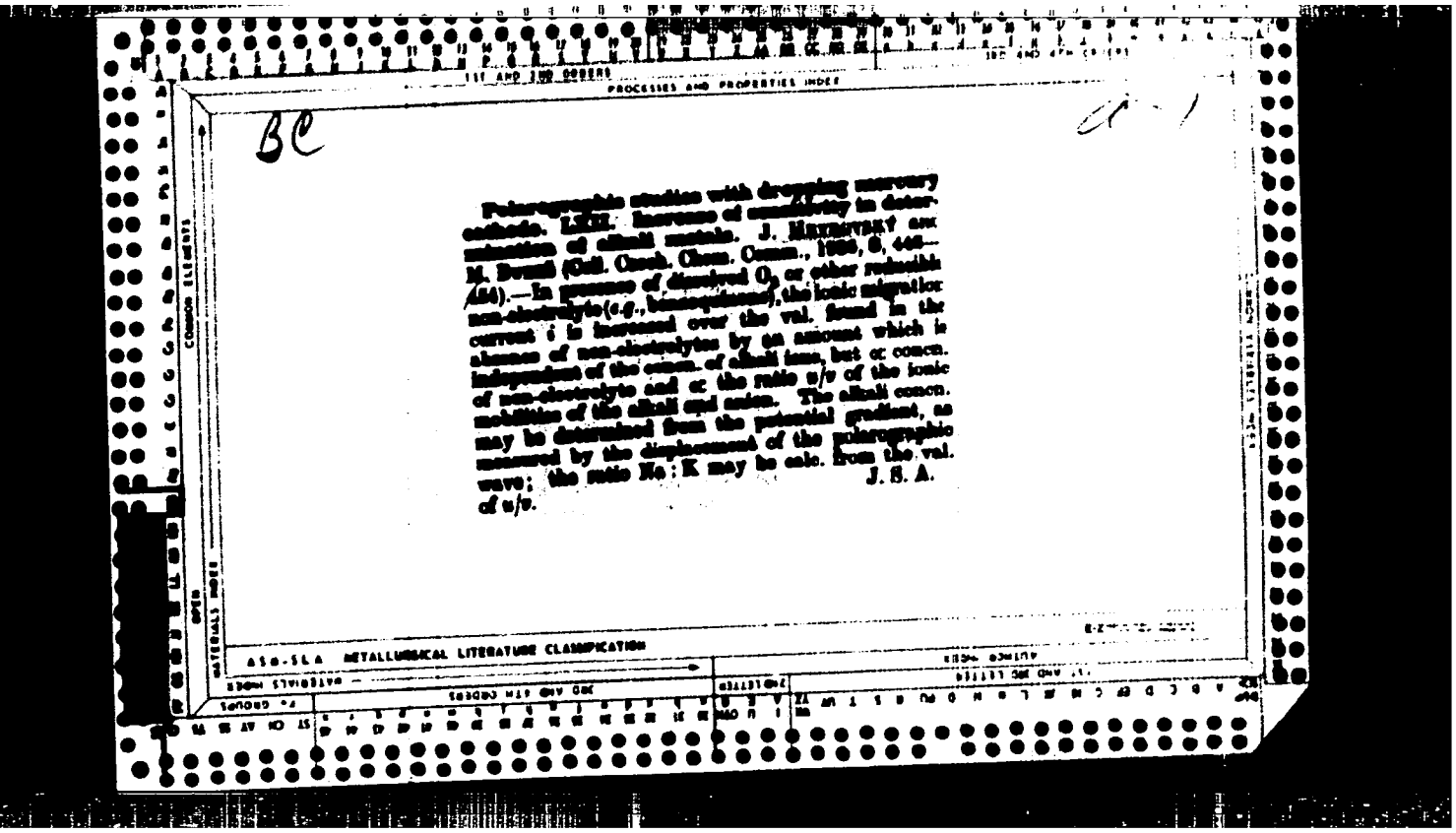
BC

A-1

Polarographic studies with the dropping mercury cathode. LVIII. Electro-reduction of dicyanogen and oxamic acid. J. Bárta and J. Heyrovský (Coll. Czech. Chem. Comm., 1936, 8, 114—124).—In aq. solutions of NaOAc, C_2N_2 causes an increase of current when the potential of the dropping Hg cathode is —1·15 volt with respect to the $N/_{10}$-Hg_2Cl_2 electrode; this is attributed to direct electro-reduction of C_2N_2. The second increase of current at —1·65 volt is probably due to electro-reduction of hexoic acid or its salt. As the age of the solutions increases, the first polarographic "wave" diminishes and the second increases. C_2N_2 has no effect on current-voltage curves of alkaline solutions, and in neutral or slightly acid solutions the second "wave" develops slowly but does not appear in more acid solutions. The results are interpreted in terms of the hydrolysis of C_2N_2. 10^{-4}—10^{-3} g.-mol. per litre of C_2N_2 and oxamic acid can be detected polarographically.

J. G. A. G.

A50-SLA METALLURGICAL LITERATURE CLASSIFICATION



Polarographic studies with dropping mercury cathode. [illegible] increase of sensitivity in determination of alkali metals. J. HEYROVSKÝ and M. Švrček (Coll. Czech. Chem. Commun., 1936, 8, 448—464).—In presence of dissolved O_2 or other reducible non-electrolyte (*e.g.*, benzoquinone), the ionic migration current *i* is increased over the val. found in the absence of non-electrolytes by an amount which is independent of the concn. of alkali ions, but ∝ concn. of non-electrolyte and ∝ the ratio u/v of the ionic mobilities of the alkali cpd anion. The alkali concn. may be determined from the potential gradient, as measured by the displacement of the polarographic wave; the ratio Na : K may be calc. from the val. of u/v. J. S. A.

HEYROVSKY, Jaroslav 1890 -

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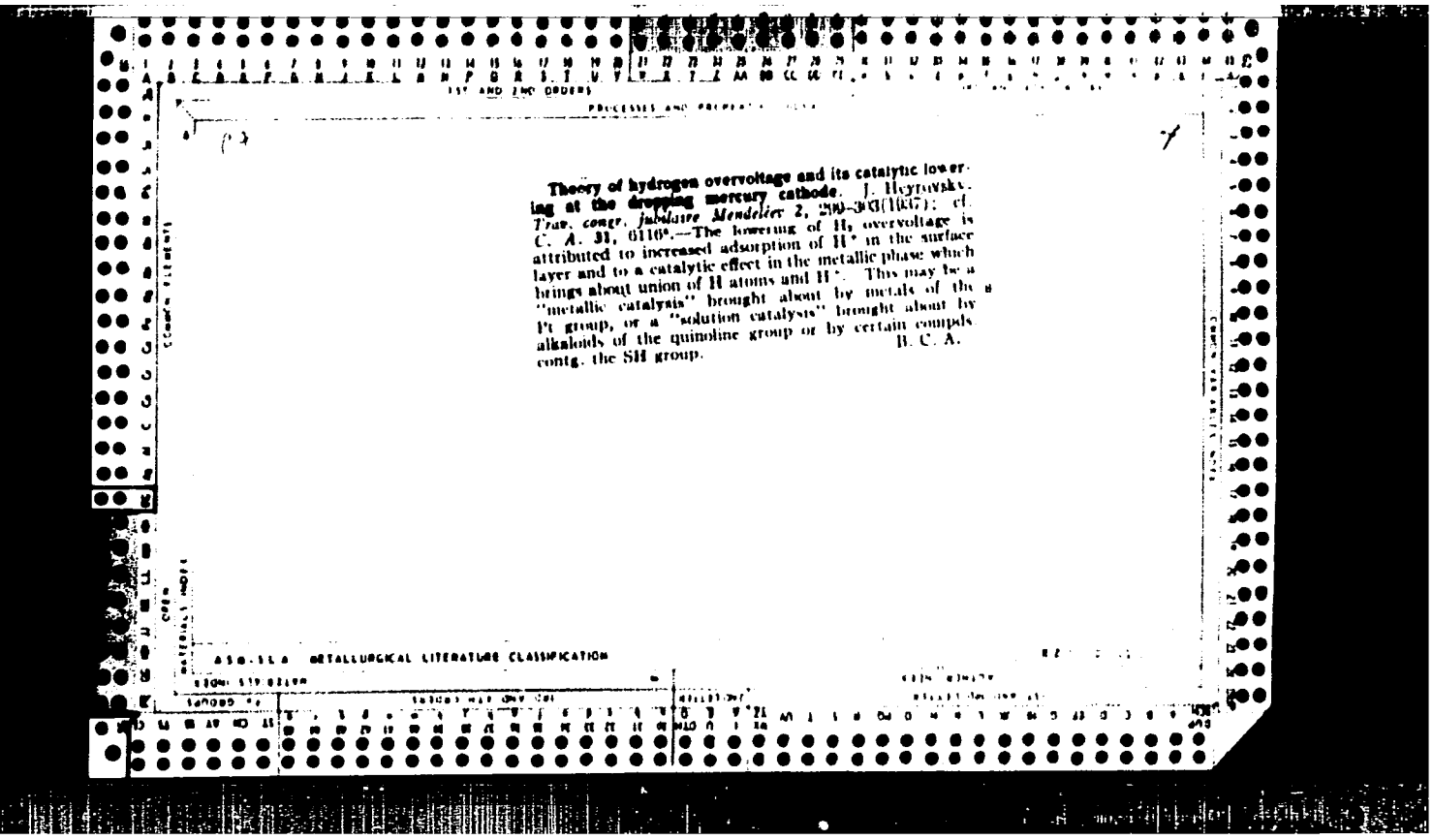
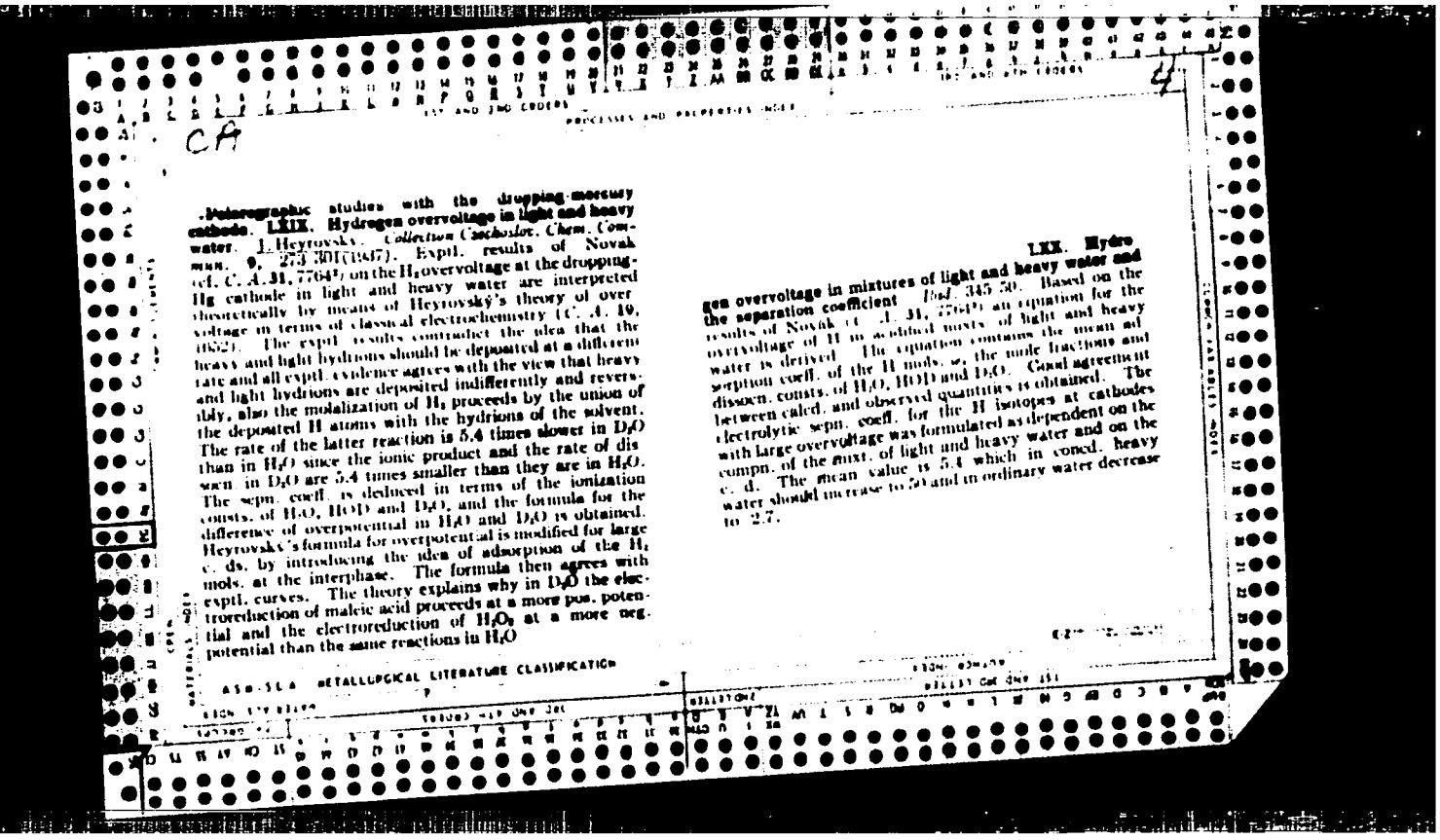


Theory of hydrogen overvoltage and its catalytic lowering at the dropping mercury cathode. J. Heyrovský. *Trav. congr. jubilaire Mendeléev* 2, 290–303(1937); cf. *C. A.* 31, 6116⁹.—The lowering of H_2 overvoltage is attributed to increased adsorption of H^+ in the surface layer and to a catalytic effect in the metallic phase which brings about union of H atoms and H^+. This may be a "metallic catalysis" brought about by metals of the Pt group, or a "solution catalysis" brought about by alkaloids of the quinoline group or by certain compds. contg. the SH group. B. C. A.

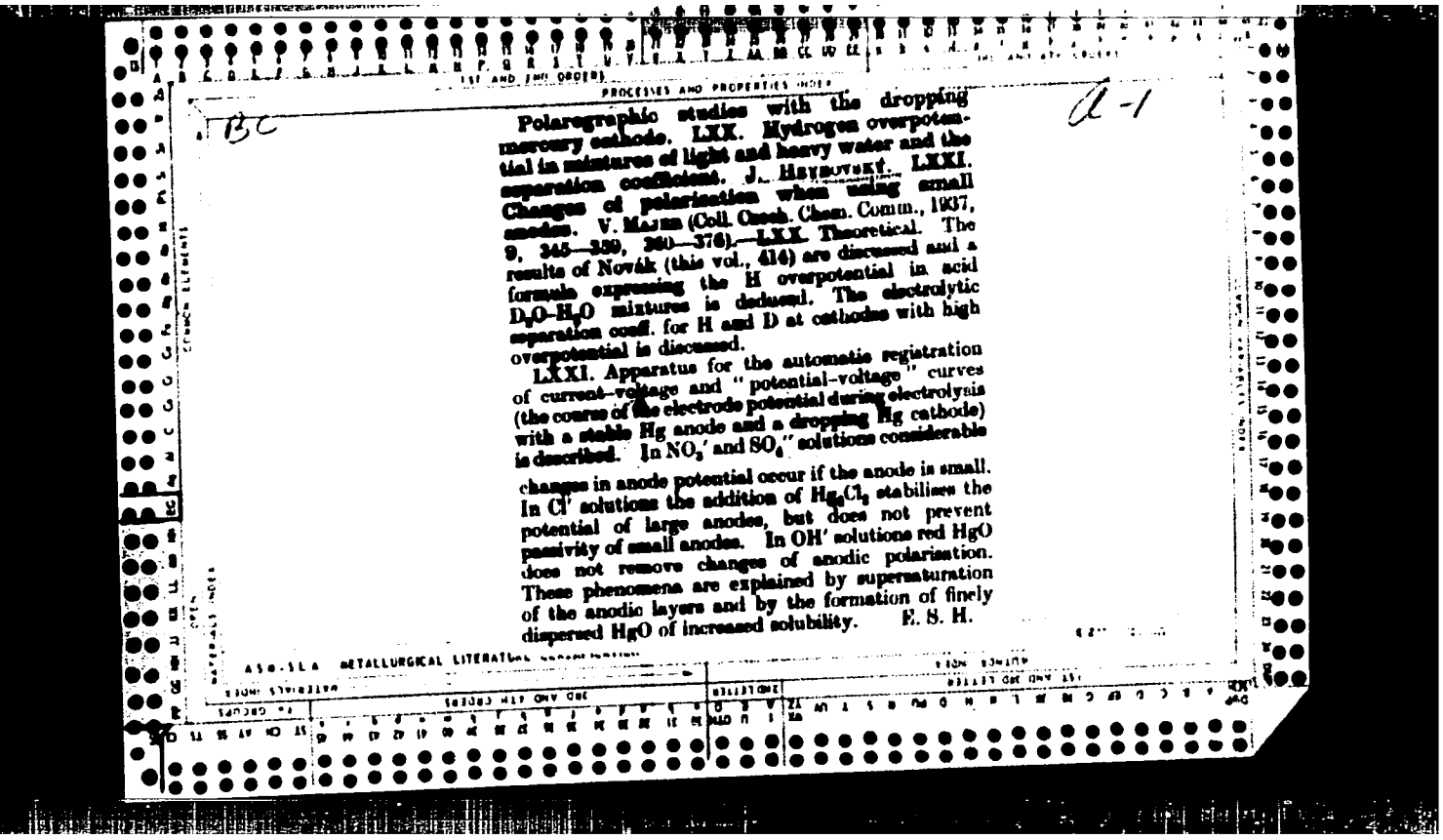


CA

Polarographic studies with the dropping-mercury cathode. LXIX. Hydrogen overvoltage in light and heavy water. J. Heyrovský. *Collection Czechoslov. Chem. Communs.* 9, 273-301(1937). Expt. results of Novák (cf. C. A. 31, 7764[1]) on the H_2 overvoltage at the dropping-Hg cathode in light and heavy water are interpreted theoretically by means of Heyrovský's theory of overvoltage in terms of classical electrochemistry (C. A. 19, 1652). The expt. results contradict the idea that the heavy and light hydrions should be deposited at a different rate and all expt. evidence agrees with the view that heavy and light hydrions are deposited indifferently and reversibly, also the molalization of H_2 proceeds by the union of the deposited H atoms with the hydrions of the solvent. The rate of the latter reaction is 5.4 times slower in D_2O than in H_2O since the ionic product and the rate of discharge in D_2O are 5.4 times smaller than they are in H_2O. The sepn. coeff. is deduced in terms of the ionization consts. of H_2O, HOD and D_2O, and the formula for the difference of overpotential in H_2O and D_2O is obtained. Heyrovský's formula for overpotential is modified for large c. ds. by introducing the idea of adsorption of the H_2 mols. at the interphase. The formula then agrees with expt. curves. The theory explains why in D_2O the electroreduction of maleic acid proceeds at a more pos. potential and the electroreduction of H_2O_2 at a more neg. potential than the same reactions in H_2O.

LXX. Hydrogen overvoltage in mixtures of light and heavy water and the separation coefficient. *Ibid.* 345-50. Based on the results of Novák (cf. *C. A.* 31, 7764[1]) an equation for the overvoltage of H in acidified mixts. of light and heavy water is derived. The equation contains the mean adsorption coeff. of the H mols., as the mole fractions and dissocn. consts. of H_2O, HOD and D_2O. Good agreement between calcd. and observed quantities is obtained. The electrolytic sepn. coeff. for the H isotopes at cathodes with large overvoltage was formulated as dependent on the compn. of the mixt. of light and heavy water and on the c. d. The mean value is 5.4 which in concd. heavy water should increase to 7.0 and in ordinary water decrease to 2.7.

A50-51A METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

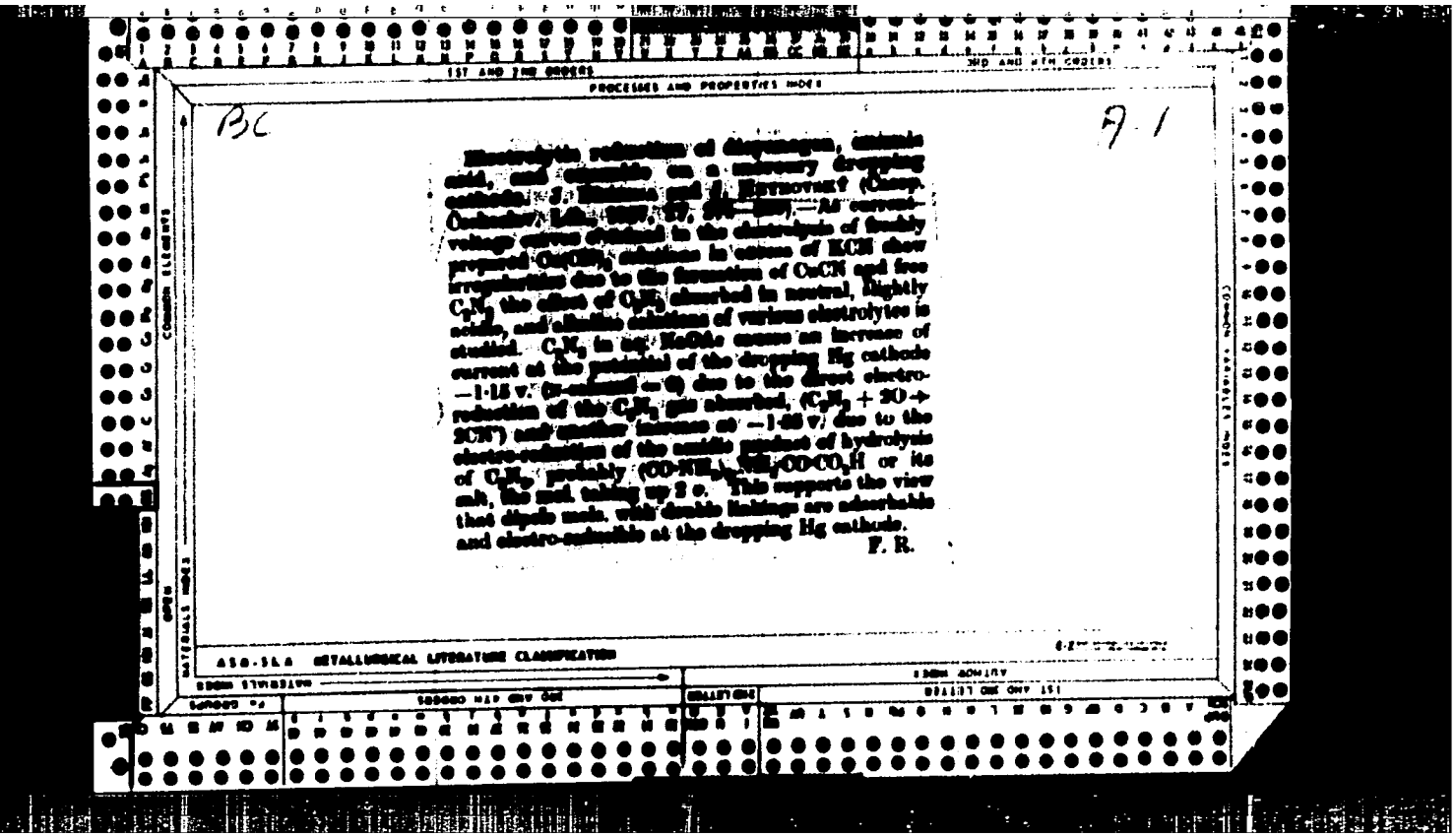
BC

A-1

Polarographic studies with the dropping mercury cathode. LXX. Hydrogen overpotential in mixtures of light and heavy water and the separation coefficient. J. Heyrovský. LXXI. Changes of polarisation when using small anodes. V. Majer (Coll. Czech. Chem. Comm., 1937, 9, 345—359, 360—376).—LXX. Theoretical. The results of Novák (this vol., 414) are discussed and a formula expressing the H overpotential in acid D_2O–H_2O mixtures is deduced. The electrolytic separation coeff. for H and D at cathodes with high overpotential is discussed.

LXXI. Apparatus for the automatic registration of current–voltage and "potential–voltage" curves (the course of the electrode potential during electrolysis with a stable Hg anode and a dropping Hg cathode) is described. In NO_3' and SO_4'' solutions considerable changes in anode potential occur if the anode is small. In Cl' solutions the addition of Hg_2Cl_2 stabilises the potential of large anodes, but does not prevent passivity of small anodes. In OH' solutions red HgO does not remove changes of anodic polarisation. These phenomena are explained by supersaturation of the anodic layers and by the formation of finely dispersed HgO of increased solubility. E. S. H.

ASM-SLA METALLURGICAL LITERATURE

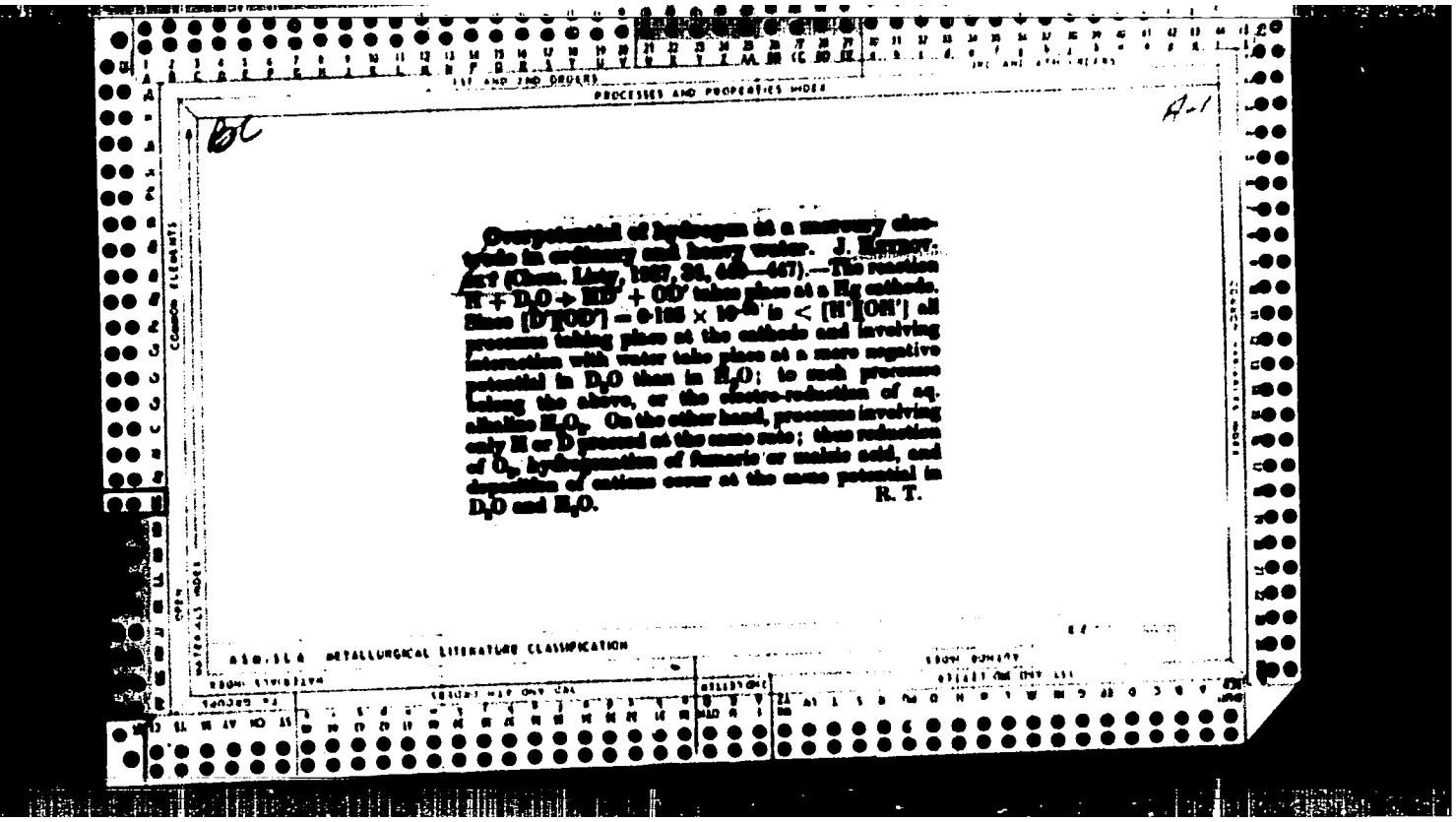


B C

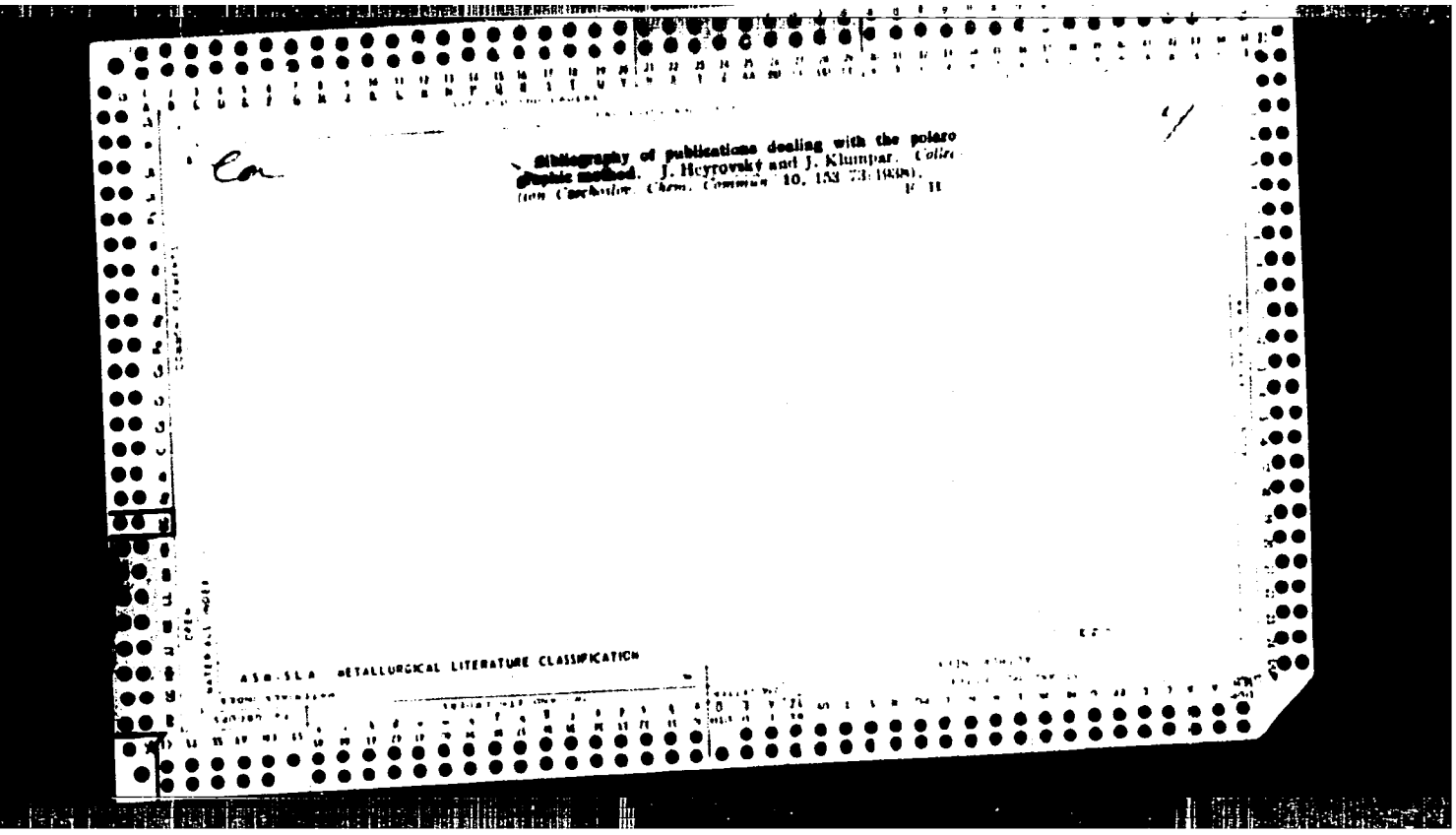
A-1

Electrolytic reduction of diazomagnesium, aminoacetic acid, and cyanamide on a mercury dropping cathode. J. Heyrovský and [illegible]. Electrochemistry (Chem. Centralblatt, 1930, 1, 2297; 57, 2[illegible]).—At current-voltage curves obtained in the electrolysis of freshly prepared $CuCl(OH)_2$ solutions in salines of KCN show irregularities due to the formation of CuCN and free C_2N_2, the effect of C_2N_2 observed in neutral, slightly acidic, and alkaline solutions of various electrolytes is studied. C_2N_2 in aq. KaOAc causes an increase of current at the potential of the dropping Hg cathode —1·15 v. (S. calomel = 0) due to the direct electro-reduction of the C_2N_2 gas absorbed, ($C_2N_2 + 2O \rightarrow 2CN^-$) and another increase at —1·65 v. due to the electro-reduction of the amidic product of hydrolysis of C_2N_2, probably $(CO\cdot NH_2)_2$, $NH_2CO\cdot CO_2H$ or its salt, the acid taking up 2 e. This supports the view that dipole mols. with double linkings are adsorbable and electro-reducible at the dropping Hg cathode.

F. R.



Overpotential of hydrogen in a mercury cathode in ordinary and heavy water. J. Kemmy, Jr. (Chem. Mag., 1937, 34, 665—667).—The reaction $H^+ + D_2O \rightarrow HD^+ + OD^-$ takes place at a Hg cathode. Since $[D^+][OD^-] = 0{\cdot}195 \times 10^{-15}$ is $< [H^+][OH^-]$ all processes taking place at the cathode and involving interaction with water take place at a more negative potential in D_2O than in H_2O; to such processes belong the above, or the electro-reduction of aq. alkaline H_2O_2. On the other hand, processes involving only H or D proceed at the same rate; thus reduction of O_2, hydrogenation of fumaric or maleic acid, and deposition of cations occur at the same potential in D_2O and H_2O. R. T.



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Les applications de la polarographie. XVIII. Congres de Chimie Industrielle a Nancy 1938. Chim. et Ind. 35, 1043 - 1050 (1938)

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(Charles University, Prague)

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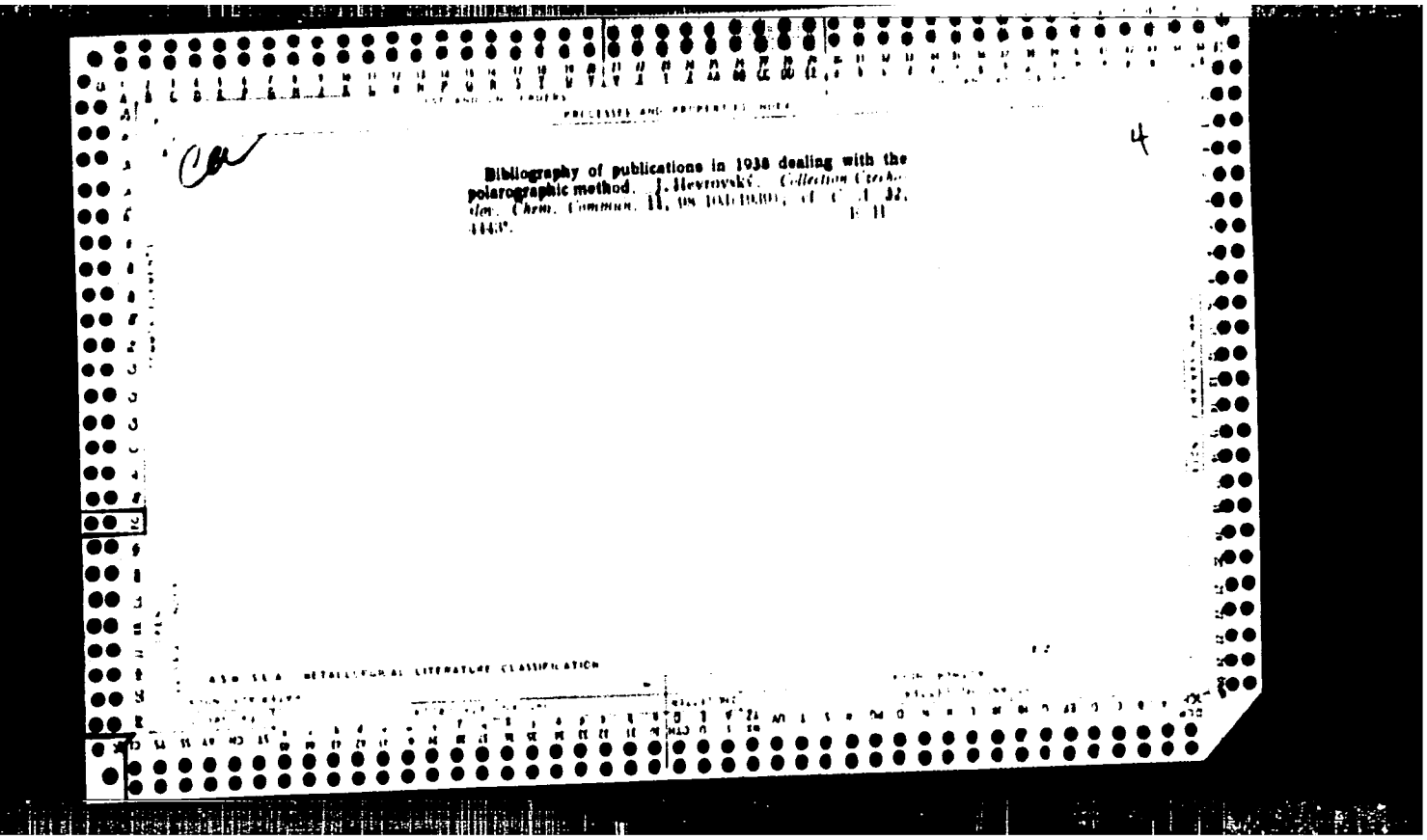

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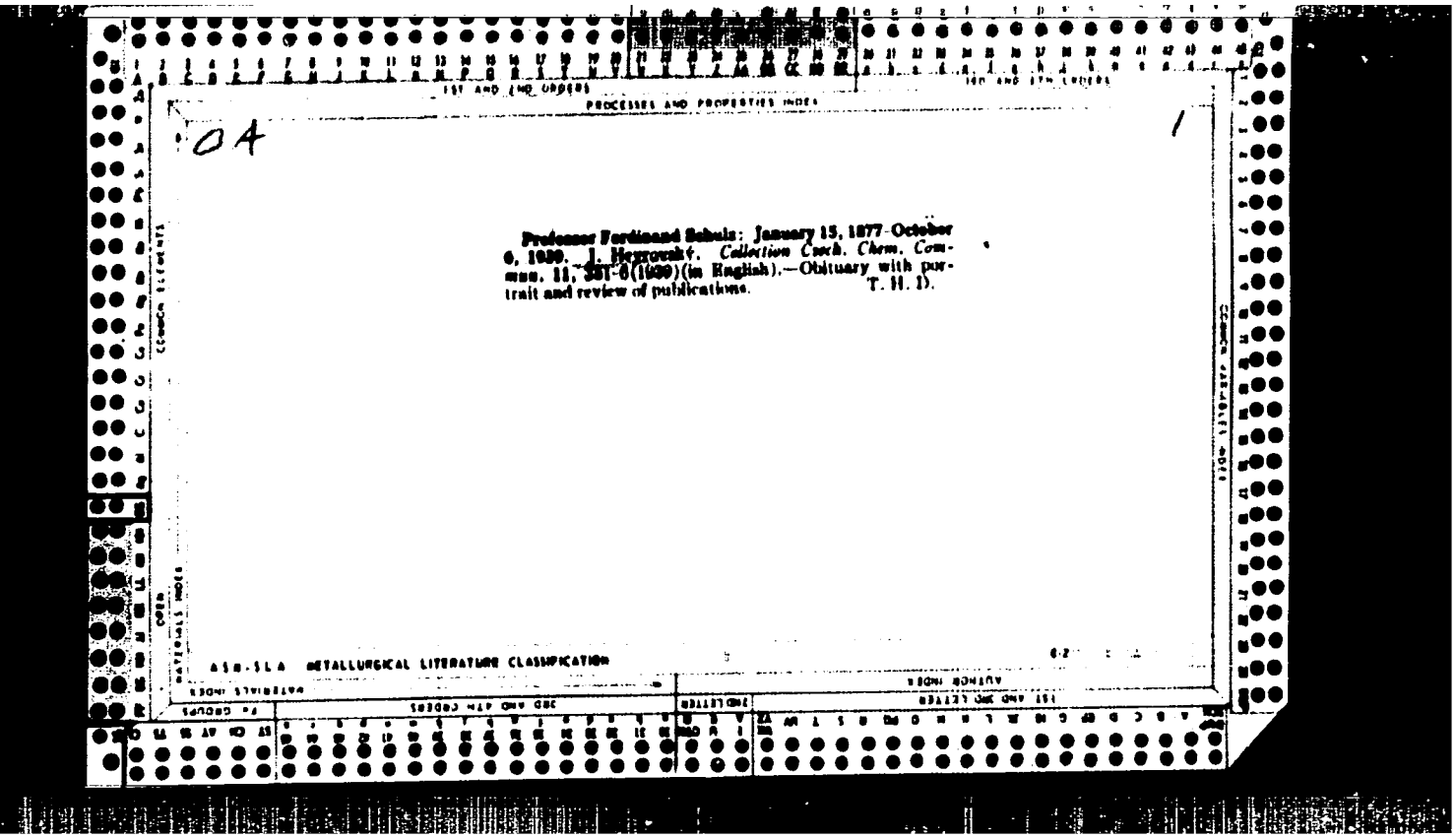

Professor Ferdinand Sebuis: January 15, 1877–October 6, 1939. J. Heyrovský. *Collection Czech. Chem. Commun.* 11, 381–6 (1939) (in English).—Obituary with portrait and review of publications. T. H. D.

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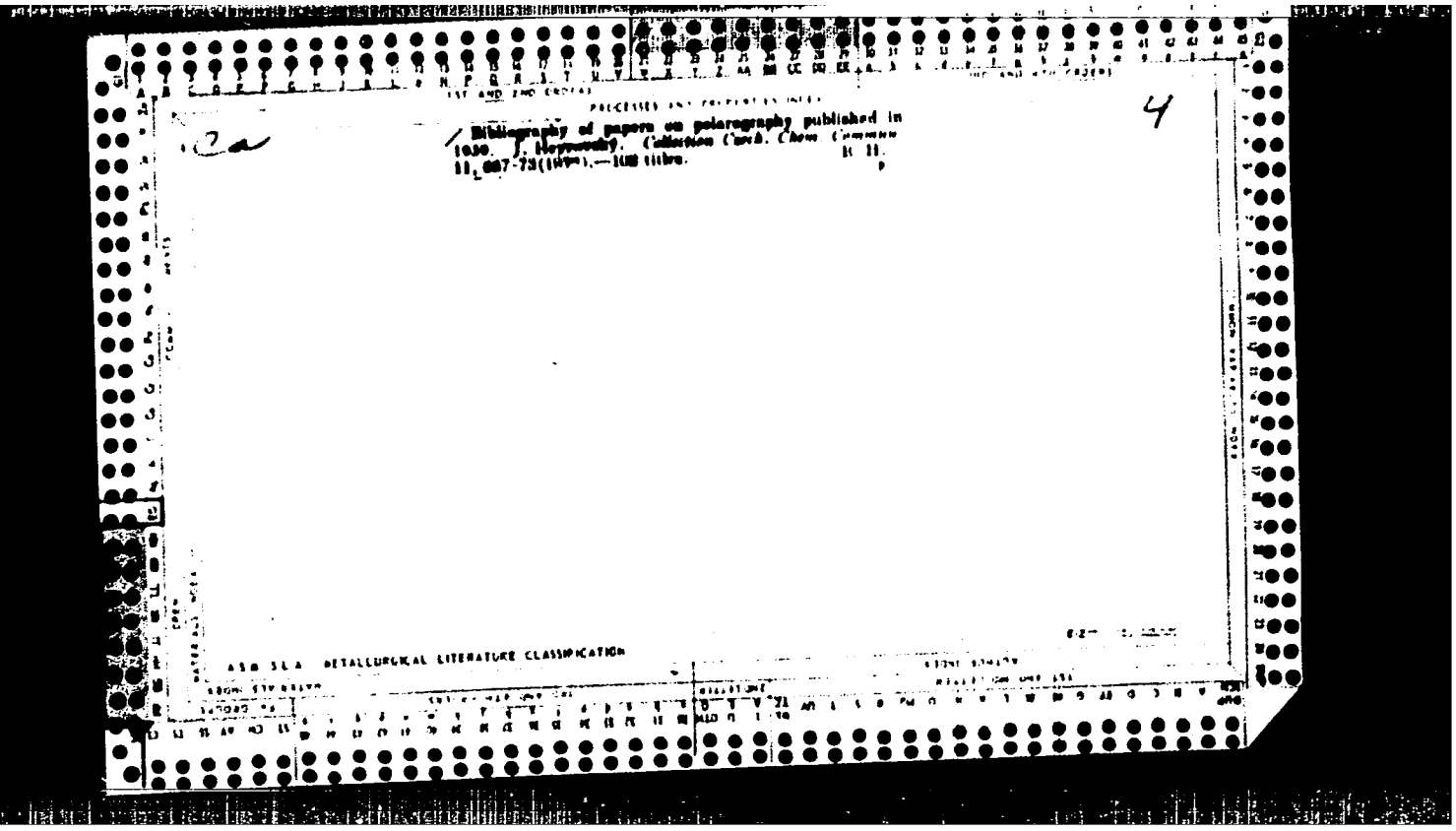
_____ and M. Kalousek: Polarographic studies with the dropping mercury electrode. Part XI. The use of dilute amalgams in the dropping electrode. Collection Czechoslav. Chem. Communications 11, 444-473 (1939)



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The electrodeposition of hydrogen and deuterium at the dropping mercury kathode. Chem. Reviews 24, 125-134 (1939).

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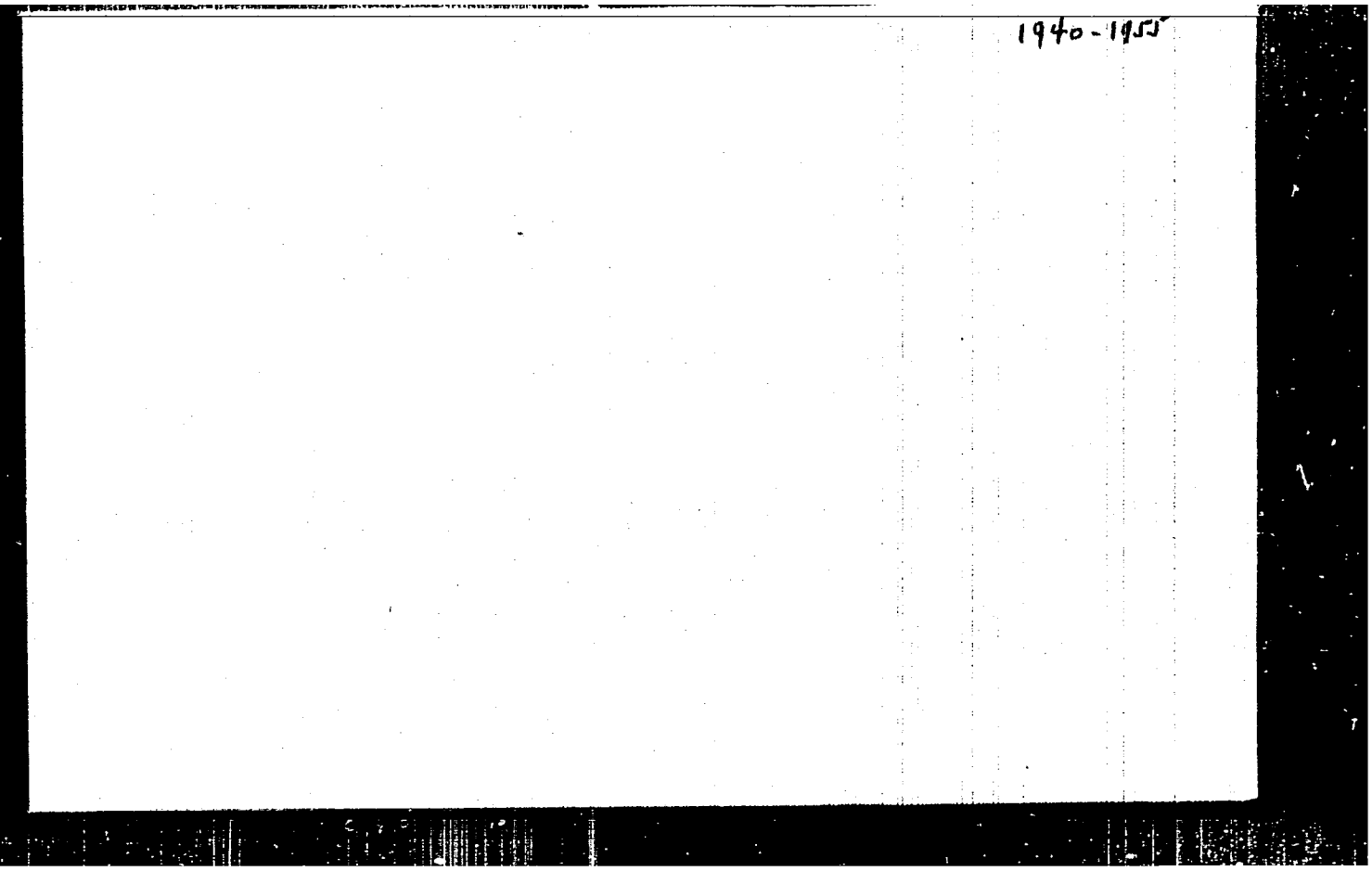

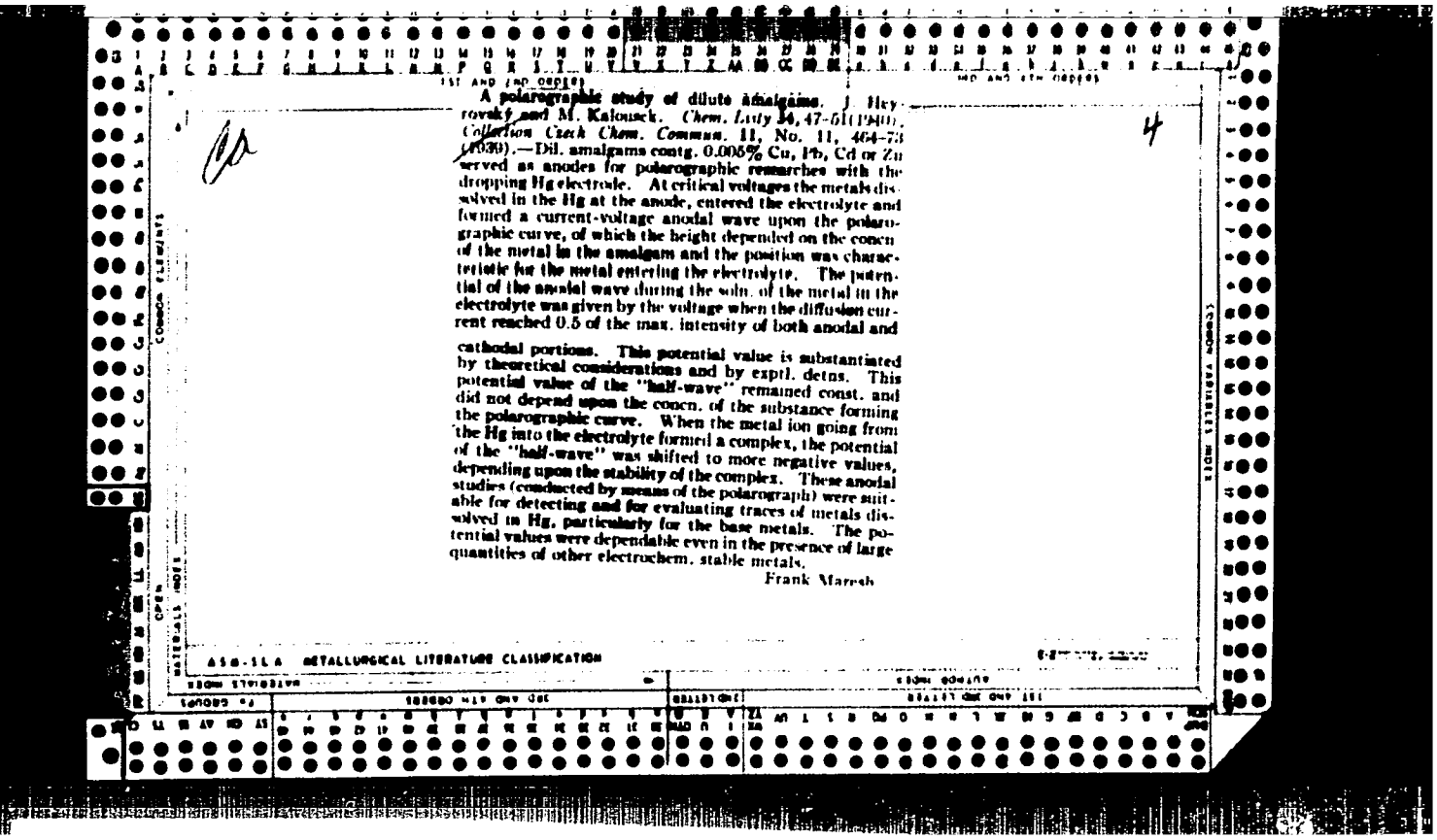

A polarographic study of dilute amalgams. J. Heyrovský and M. Kalousek. *Chem. Listy* 34, 47-51 (1940). *Collection Czech. Chem. Commun.* 11, No. 11, 464-73 (1939).—Dil. amalgams contg. 0.005% Cu, Pb, Cd or Zn served as anodes for polarographic researches with the dropping Hg electrode. At critical voltages the metals dissolved in the Hg at the anode, entered the electrolyte and formed a current-voltage anodal wave upon the polarographic curve, of which the height depended on the concn. of the metal in the amalgam and the position was characteristic for the metal entering the electrolyte. The potential of the anodal wave during the soln. of the metal in the electrolyte was given by the voltage when the diffusion current reached 0.5 of the max. intensity of both anodal and cathodal portions. This potential value is substantiated by theoretical considerations and by exptl. detns. This potential value of the "half-wave" remained const. and did not depend upon the concn. of the substance forming the polarographic curve. When the metal ion going from the Hg into the electrolyte formed a complex, the potential of the "half-wave" was shifted to more negative values, depending upon the stability of the complex. These anodal studies (conducted by means of the polarograph) were suitable for detecting and for evaluating traces of metals dissolved in Hg, particularly for the base metals. The potential values were dependable even in the presence of large quantities of other electrochem. stable metals.

Frank Marsh

A 56-1 LA METALLURGICAL LITERATURE CLASSIFICATION

HEYROVSKY, Jaroslav 1890 -

Polarographic analysis
Chicago, Ill., E. H. Sargent & Co., c1941 - 39 p.

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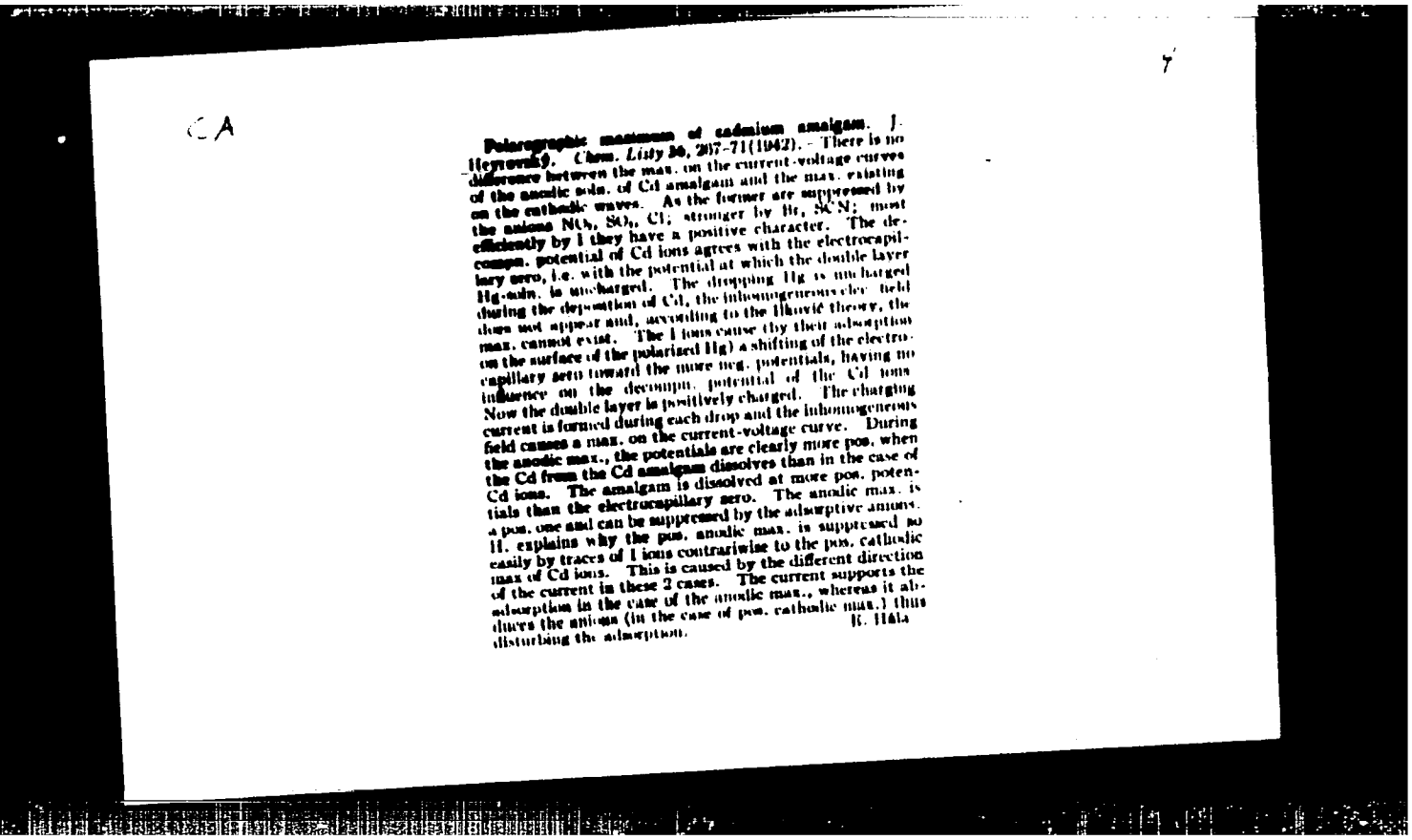
The polarographic reduction of osmium tetroxide. W. P. Crowell and Heyrovsky, J. and D. W. Engelkemeir. J. Am. Chem Soc. 63, 2848-90 (1941)

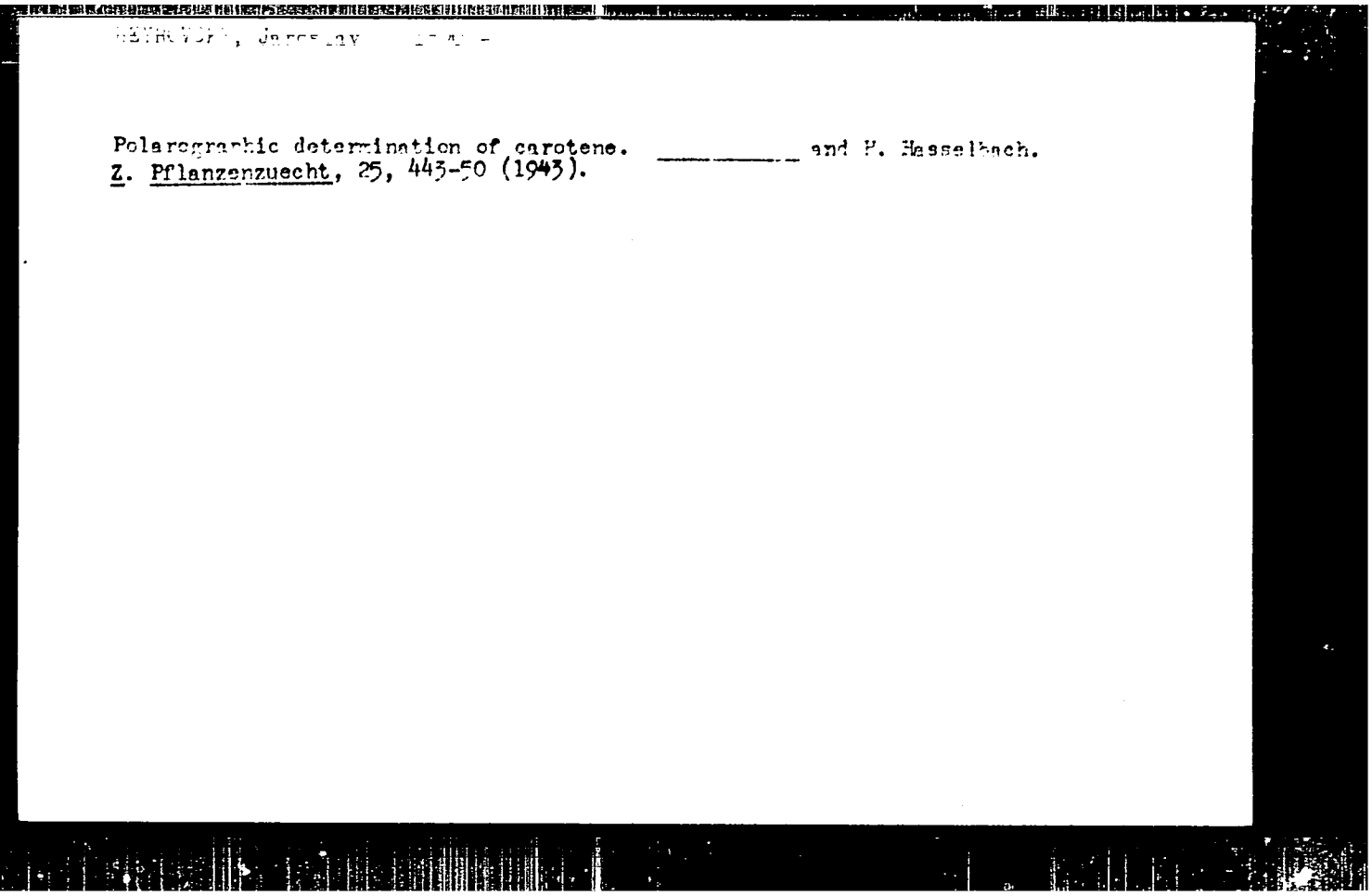
HEYROVSKY, Jaroslav 1890 -

Polarographie; theoretische grundlagen, praktische ausfuehrung und anwendungen der elektrolyse mit der tropfenden quecksilberelektrode . . . Wien, J. Springer, 1941. 8 + 514 p. - Illus. Polorographisches schriftum, p. 427-82. Lithoprinted by Edwards Bros., Ann Arbor, 1944



CA

Polarographic maximum of cadmium amalgam. J. Heyrovský. *Chem. Listy* 36, 207–71(1942). – There is no difference between the max. on the current-voltage curves of the anodic sol'n. of Cd amalgam and the max. existing on the cathodic waves. As the former are suppressed by the anions NO_3, SO_4, Cl; stronger by Br, SCN; most efficiently by I they have a positive character. The decompn. potential of Cd ions agrees with the electrocapillary zero, i.e. with the potential at which the double layer Hg-soln. is uncharged. The dropping Hg is uncharged during the deposition of Cd, the inhomogeneous elec. field does not appear and, according to the Ilkovič theory, the max. cannot exist. The I ions cause (by their adsorption on the surface of the polarized Hg) a shifting of the electrocapillary zero toward the more neg. potentials, having no influence on the decompn. potential of the Cd ions. Now the double layer is positively charged. The charging current is formed during each drop and the inhomogeneous field causes a max. on the current-voltage curve. During the anodic max., the potentials are clearly more pos. when the Cd from the Cd amalgam dissolves than in the case of Cd ions. The amalgam is dissolved at more pos. potentials than the electrocapillary zero. The anodic max. is a pos. one and can be suppressed by the adsorptive anions. H. explains why the pos. anodic max. is suppressed so easily by traces of I ions contrariwise to the pos. cathodic max of Cd ions. This is caused by the different direction of the current in these 2 cases. The current supports the adsorption in the case of the anodic max., whereas it abduces the anions (in the case of pos. cathodic max.) thus disturbing the adsorption. B. Hála



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Polarographic determination of carotene. _____ and P. Hasselbach. Z. Pflanzenzuecht, 25, 443-50 (1943).

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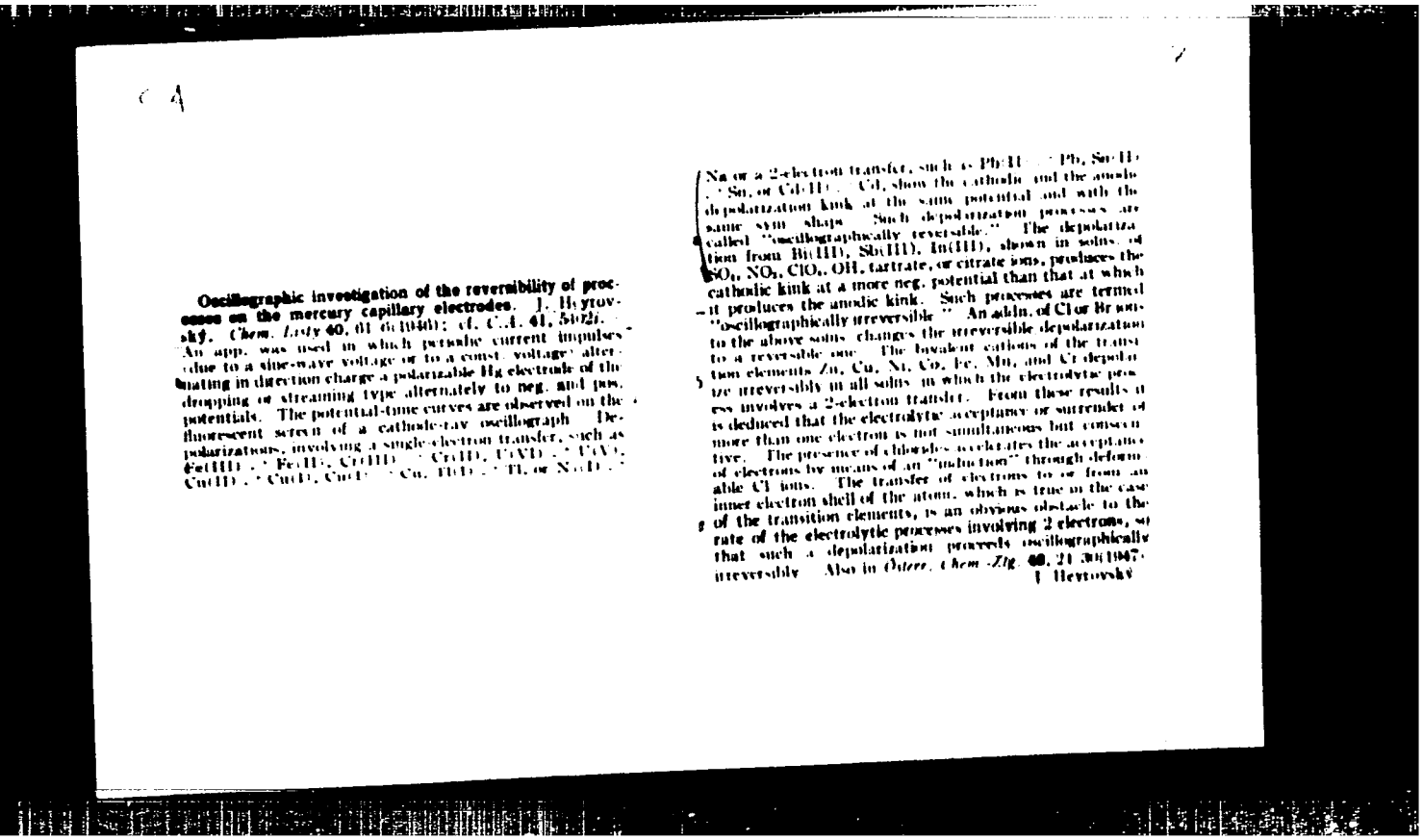
_____ and J. Forejt. Oscillographic polarography. Z. physik. Chem. 195, 77-96 (1943)

HEYROVSKY, Jaroslav 1890 -

Fundamentals and metallurgical importance of polarography. Metallwirtschaft 23, 353-41 (1944)

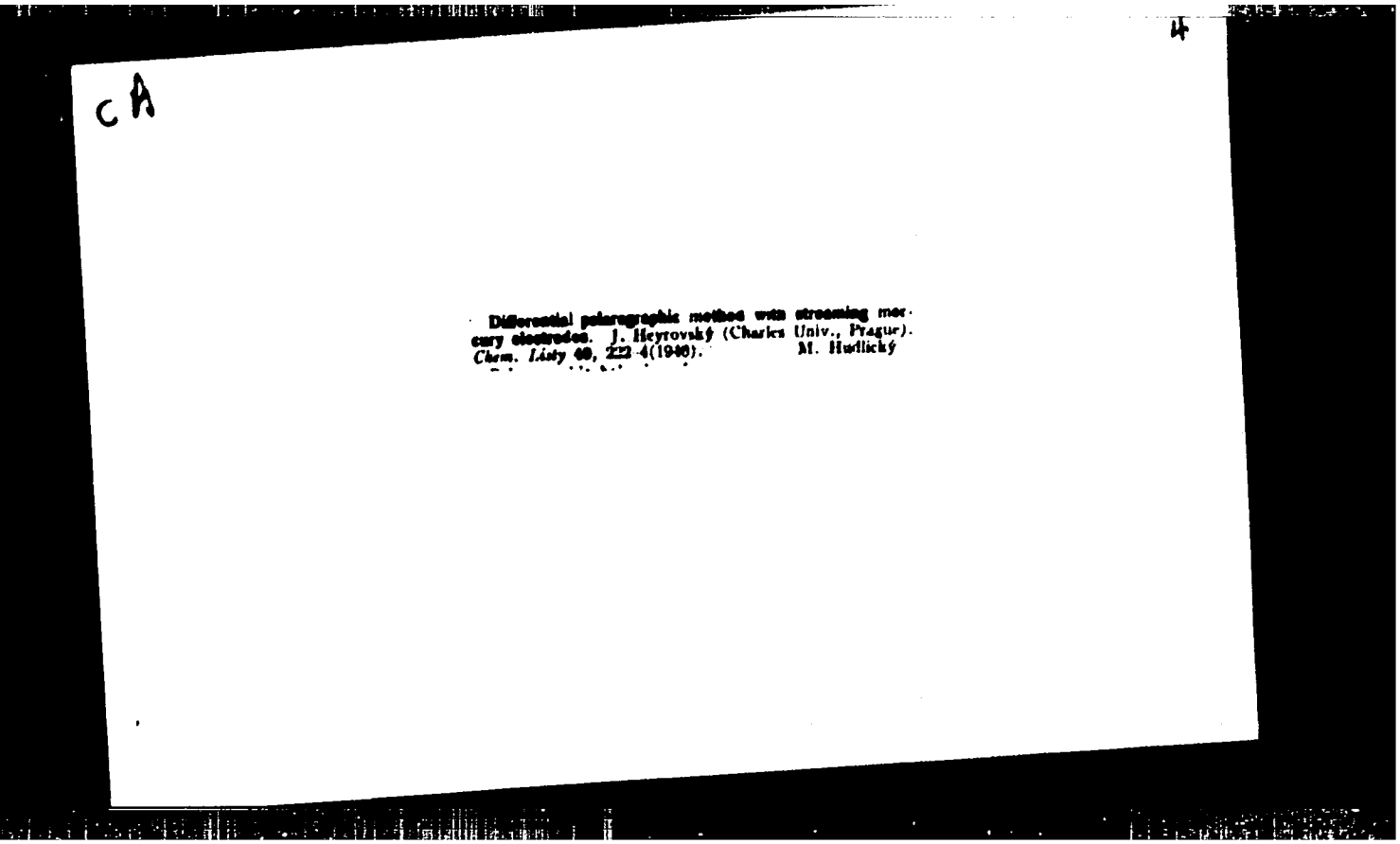
HEYROVSKY, Jaroslav 1890 -

Progress of polarography in the year 1941. Mikrochemie ver. Mikrochim. Acta 32, 103-22 (1944)



C A

Oscillographic investigation of the reversibility of processes on the mercury capillary electrodes. J. Heyrovsky. *Chem. Listy* **40**, 61 6 (1946); cf. C.A. **41**, 5072*i*. An app. was used in which periodic current impulses due to a sine-wave voltage or to a const. voltage alternating in direction charge a polarizable Hg electrode of the dropping or streaming type alternately to neg. and pos. potentials. The potential-time curves are observed on the fluorescent screen of a cathode-ray oscillograph. Depolarizations, involving a single-electron transfer, such as Fe(III) → Fe(II), Cr(III) → Cr(II), U(VI) → U(V), Cu(II) → Cu(I), Cu(I) → Cu, Tl(I) → Tl, or Na(I) → Na, or a 2-electron transfer, such as Pb(II) → Pb, Sn(II) → Sn, or Cd(II) → Cd, show the cathodic and the anodic depolarization kink at the same potential and with the same sym. shape. Such depolarization processes are called "oscillographically reversible." The depolarization from Bi(III), Sb(III), In(III), shown in solns. of SO_4, NO_3, ClO_4, OH, tartrate, or citrate ions, produces the cathodic kink at a more neg. potential than that at which it produces the anodic kink. Such processes are termed "oscillographically irreversible." An addn. of Cl or Br ions to the above solns. changes the irreversible depolarization to a reversible one. The bivalent cations of the transition elements Zn, Cu, Ni, Co, Fe, Mn, and Cr depolarize irreversibly in all solns. in which the electrolytic process involves a 2-electron transfer. From these results it is deduced that the electrolytic acceptance or surrender of more than one electron is not simultaneous but consecutive. The presence of chlorides accelerates the acceptance of electrons by means of an "induction" through deformable Cl ions. The transfer of electrons to or from an inner electron shell of the atom, which is true in the case of the transition elements, is an obvious obstacle to the rate of the electrolytic processes involving 2 electrons, so that such a depolarization proceeds oscillographically irreversibly. Also in *Collect. Chem. Zig.* **60**, 21 30 (1947). J. Heyrovsky



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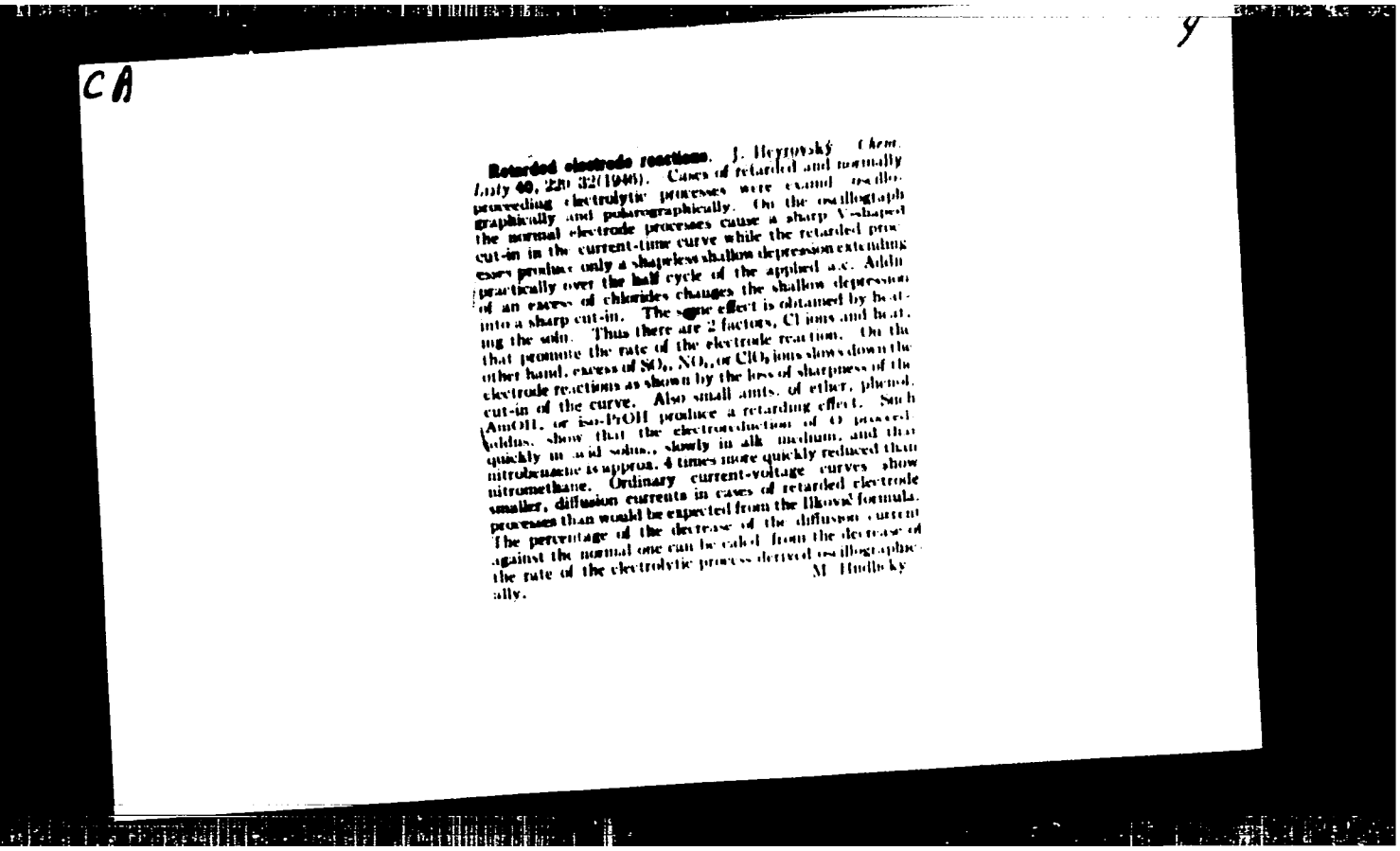
CA

Differential polarographic method with streaming mercury electrodes. J. Heyrovský (Charles Univ., Prague). *Chem. Listy* 40, 222-4(1946). M. Hudlický

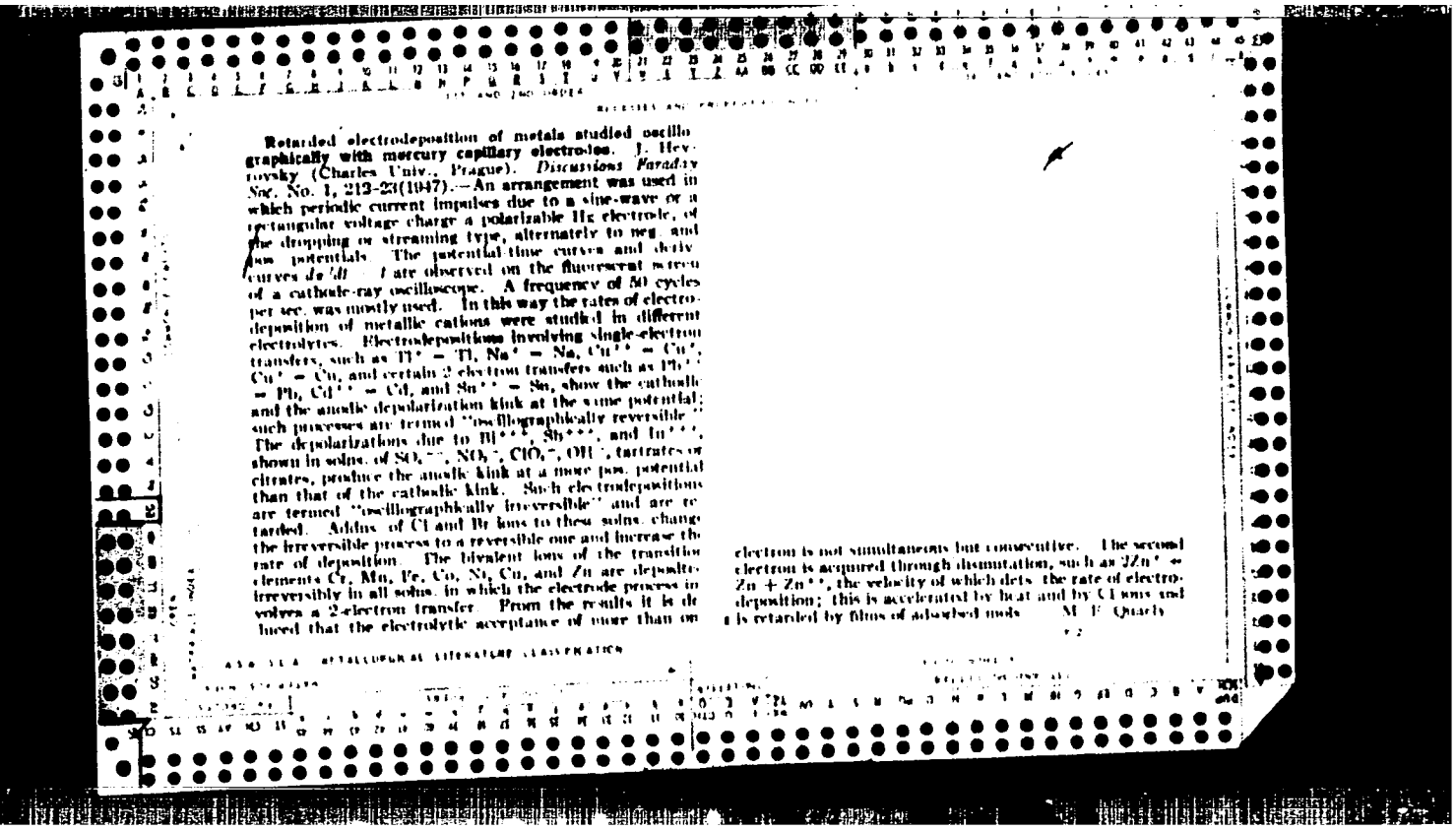


CA

4

Retarded electrode reactions. J. Heyrovský *Chem. Listy* **40**, 230–32(1946). Cases of retarded and normally proceeding electrolytic processes were examd. oscillographically and polarographically. On the oscillograph the normal electrode processes cause a sharp V-shaped cut-in in the current-time curve while the retarded processes produce only a shapeless shallow depression extending practically over the half cycle of the applied a.c. Addn. of an excess of chlorides changes the shallow depression into a sharp cut-in. The same effect is obtained by heating the soln. Thus there are 2 factors, Cl ions and heat, that promote the rate of the electrode reaction. On the other hand, excess of SO_4, NO_3, or ClO_3 ions slows down the electrode reactions as shown by the loss of sharpness of the cut-in of the curve. Also small amts. of ether, phenol, AmOH, or iso-PrOH produce a retarding effect. Such acids, show that the electroreduction of O proceeds quickly in acid solns., slowly in alk. medium, and that nitrobenzene is approx. 4 times more quickly reduced than nitromethane. Ordinary current-voltage curves show smaller, diffusion currents in cases of retarded electrode processes than would be expected from the Ilkovič formula. The percentage of the decrease of the diffusion current against the normal one can be calcd. from the decrease of the rate of the electrolytic process derived oscillographically.

M. Hudlický



Retarded electrodeposition of metals studied oscillographically with mercury capillary electrodes. J. Heyrovsky (Charles Univ., Prague). *Discussions Faraday Soc.* No. 1, 213-23(1947).—An arrangement was used in which periodic current impulses due to a sine-wave or a rectangular voltage charge a polarizable Hg electrode, of the dropping or streaming type, alternately to neg. and pos. potentials. The potential-time curves and derivative curves dv/dt = f are observed on the fluorescent screen of a cathode-ray oscilloscope. A frequency of 50 cycles per sec. was mostly used. In this way the rates of electrodeposition of metallic cations were studied in different electrolytes. Electrodepositions involving single-electron transfers, such as $Tl^+ \rightarrow Tl$, $Na^+ \rightarrow Na$, $Cu^{++} \rightarrow Cu^+$, $Cu^+ \rightarrow Cu$, and certain 2-electron transfers such as $Pb^{++} \rightarrow Pb$, $Cd^{++} \rightarrow Cd$, and $Sn^{++} \rightarrow Sn$, show the cathodic and the anodic depolarization kink at the same potential; such processes are termed "oscillographically reversible." The depolarizations due to Bi^{+++}, Sb^{+++}, and In^{+++}, shown in solns. of SO_4^{--}, NO_3^-, ClO_4^-, OH^-, tartrates or citrates, produce the anodic kink at a more pos. potential than that of the cathodic kink. Such electrodepositions are termed "oscillographically irreversible" and are retarded. Additions of Cl and Br ions to these solns. change the irreversible process to a reversible one and increase the rate of deposition. The divalent ions of the transition elements Cr, Mn, Fe, Co, Ni, Cu, and Zn are deposited irreversibly in all solns. in which the electrode process involves a 2-electron transfer. From the results it is deduced that the electrolytic acceptance of more than one electron is not simultaneous but consecutive. The second electron is acquired through dismutation, such as $2Zn^+ \rightarrow Zn + Zn^{++}$, the velocity of which dets. the rate of electrodeposition; this is accelerated by heat and by Cl ions and is retarded by films of adsorbed mols. M. F. Quayle

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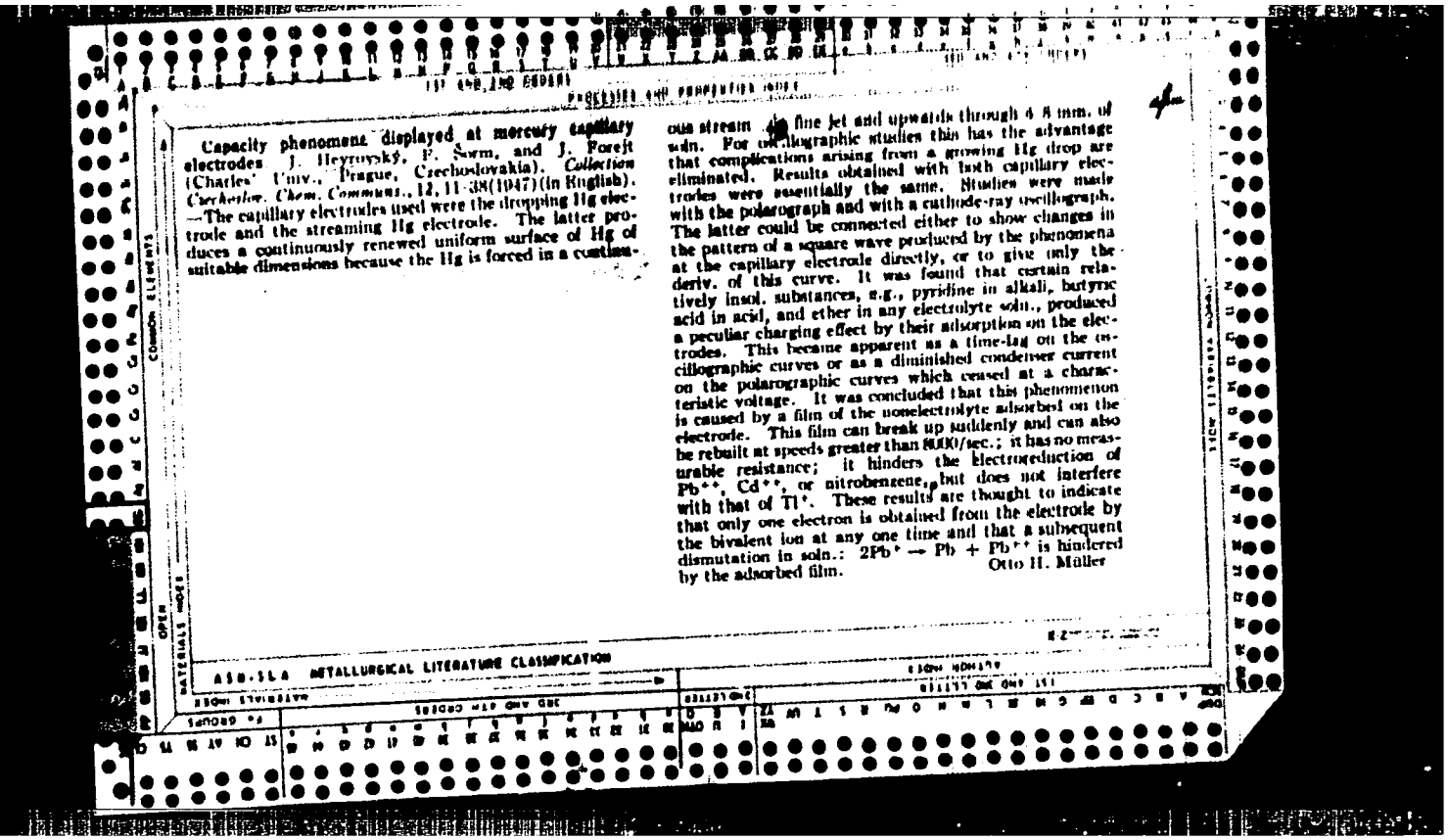
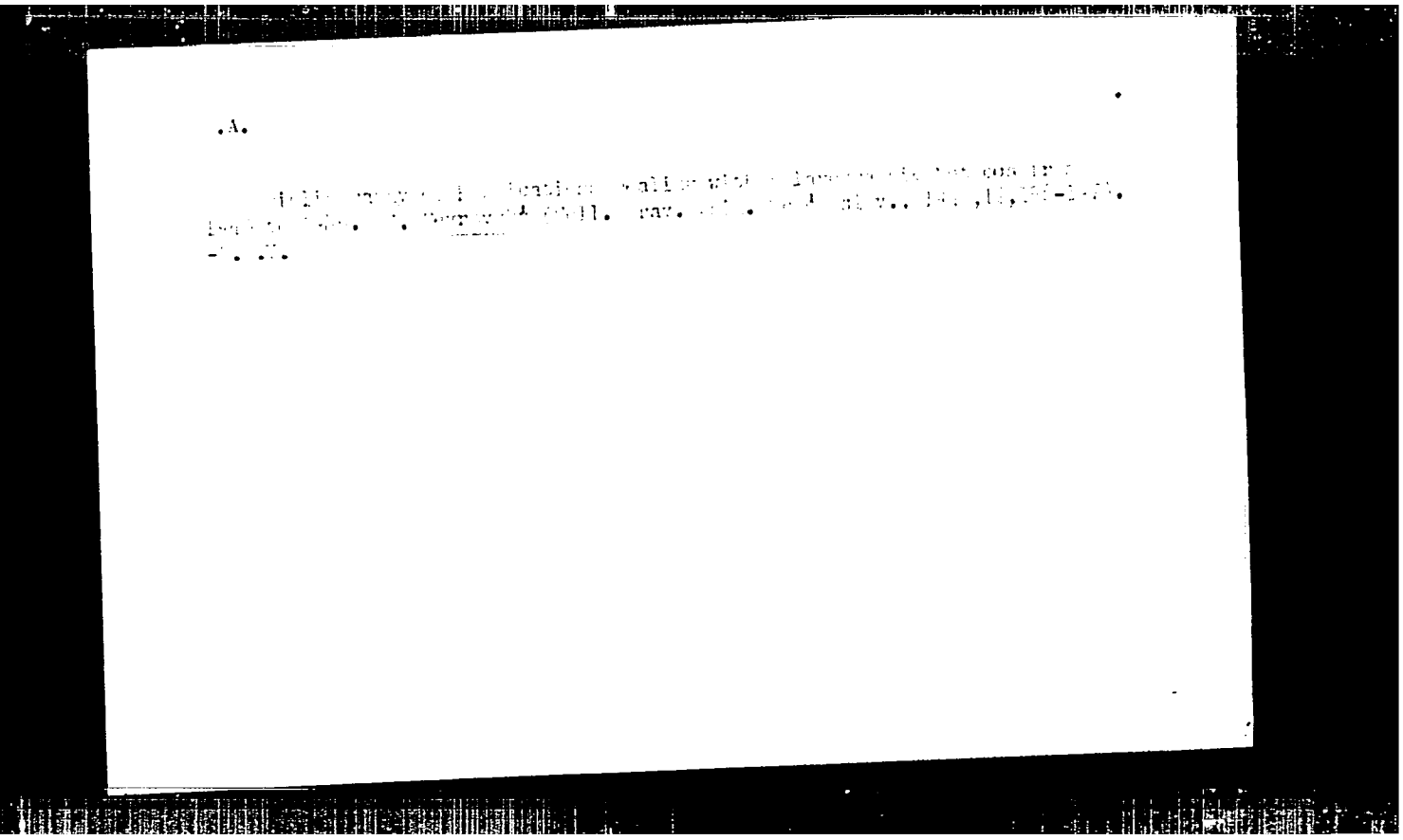
Use of oscillographic potential-time curves in polarography. Proc. Intern. Congr. Pure and Applied Chem. (London) 11, 491-94 (1947) (in English)



Capacity phenomena displayed at mercury capillary electrodes J. Heyrovský, F. Šorm, and J. Forejt (Charles' Univ., Prague, Czechoslovakia). *Collection Czechoslov. Chem. Communs.*, 12, 11-38(1947)(in English). —The capillary electrodes used were the dropping Hg electrode and the streaming Hg electrode. The latter produces a continuously renewed uniform surface of Hg of suitable dimensions because the Hg is forced in a continuous stream thru fine jet and upwards through 4-8 mm. of soln. For oscillographic studies this has the advantage that complications arising from a growing Hg drop are eliminated. Results obtained with both capillary electrodes were essentially the same. Studies were made with the polarograph and with a cathode-ray oscillograph. The latter could be connected either to show changes in the pattern of a square wave produced by the phenomena at the capillary electrode directly, or to give only the deriv. of this curve. It was found that certain relatively insol. substances, e.g., pyridine in alkali, butyric acid in acid, and ether in any electrolyte soln., produced a peculiar charging effect by their adsorption on the electrodes. This became apparent as a time-lag on the oscillographic curves or as a diminished condenser current on the polarographic curves which ceased at a characteristic voltage. It was concluded that this phenomenon is caused by a film of the nonelectrolyte adsorbed on the electrode. This film can break up suddenly and can also be rebuilt at speeds greater than 8000/sec.; it has no measurable resistance; it hinders the electroreduction of Pb^{++}, Cd^{++}, or nitrobenzene, but does not interfere with that of Tl^{+}. These results are thought to indicate that only one electron is obtained from the electrode by the bivalent ion at any one time and that a subsequent dismutation in soln.: $2Pb^{+} \rightarrow Pb + Pb^{++}$ is hindered by the adsorbed film.

Otto H. Müller



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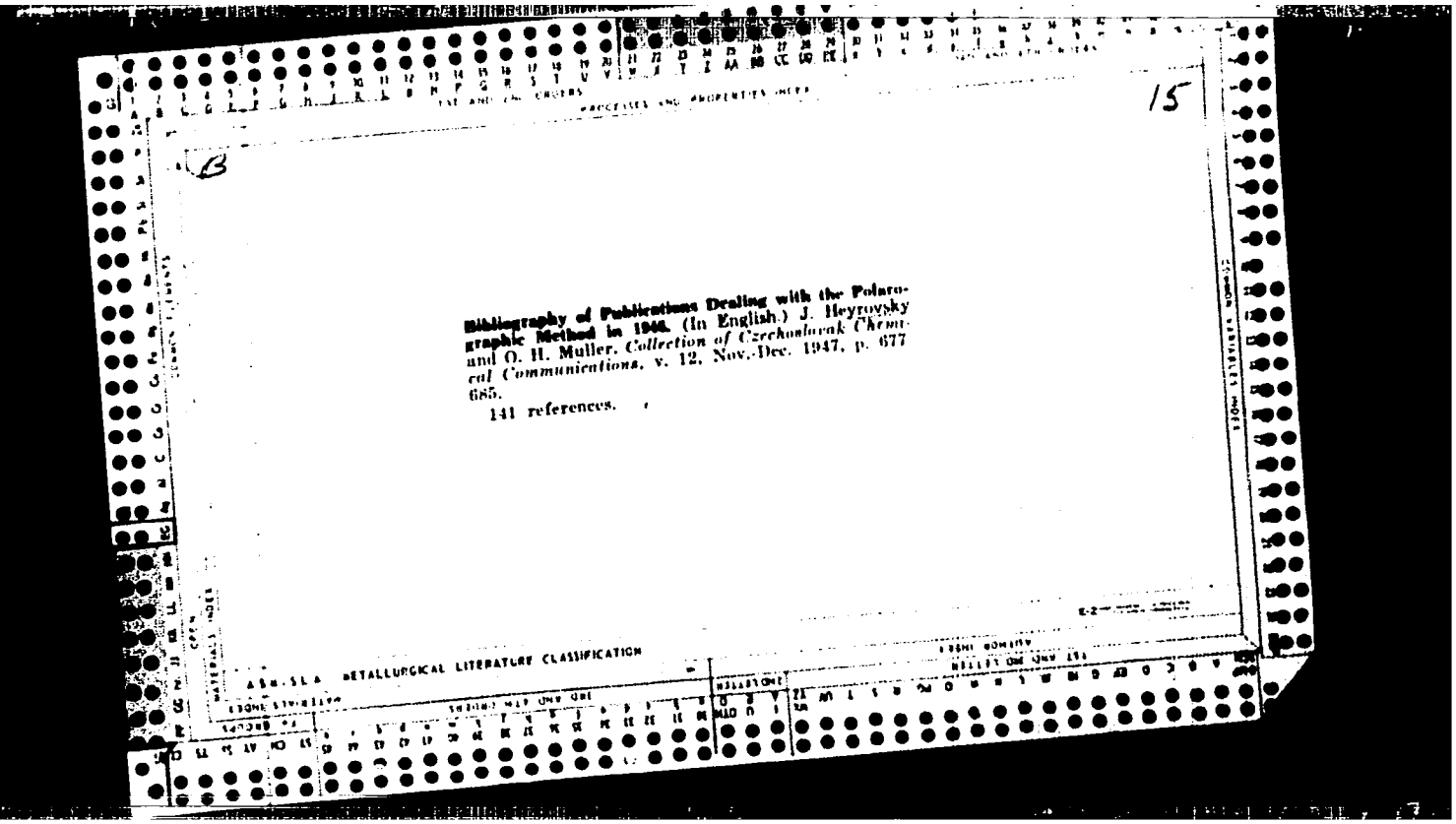

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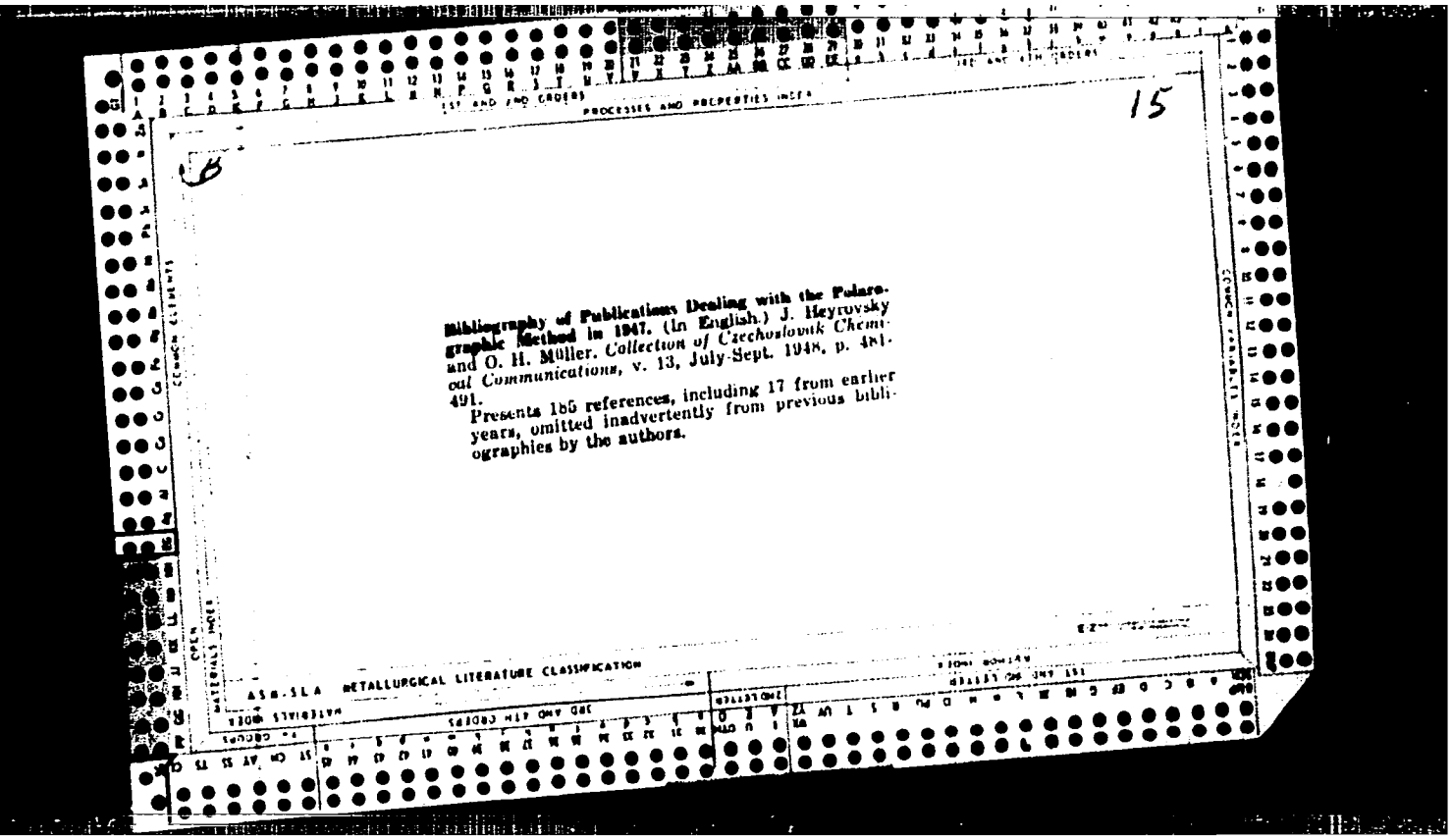

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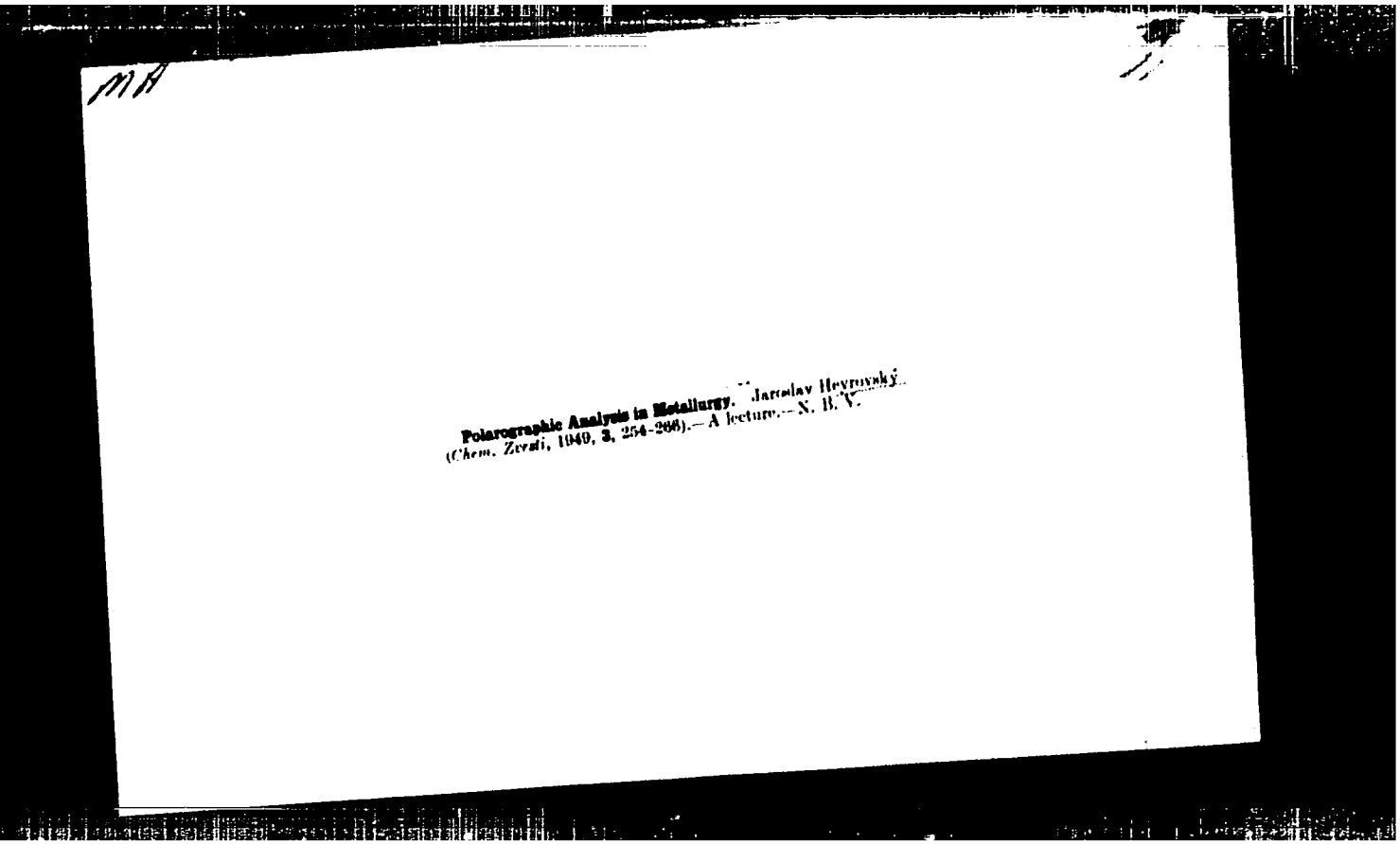

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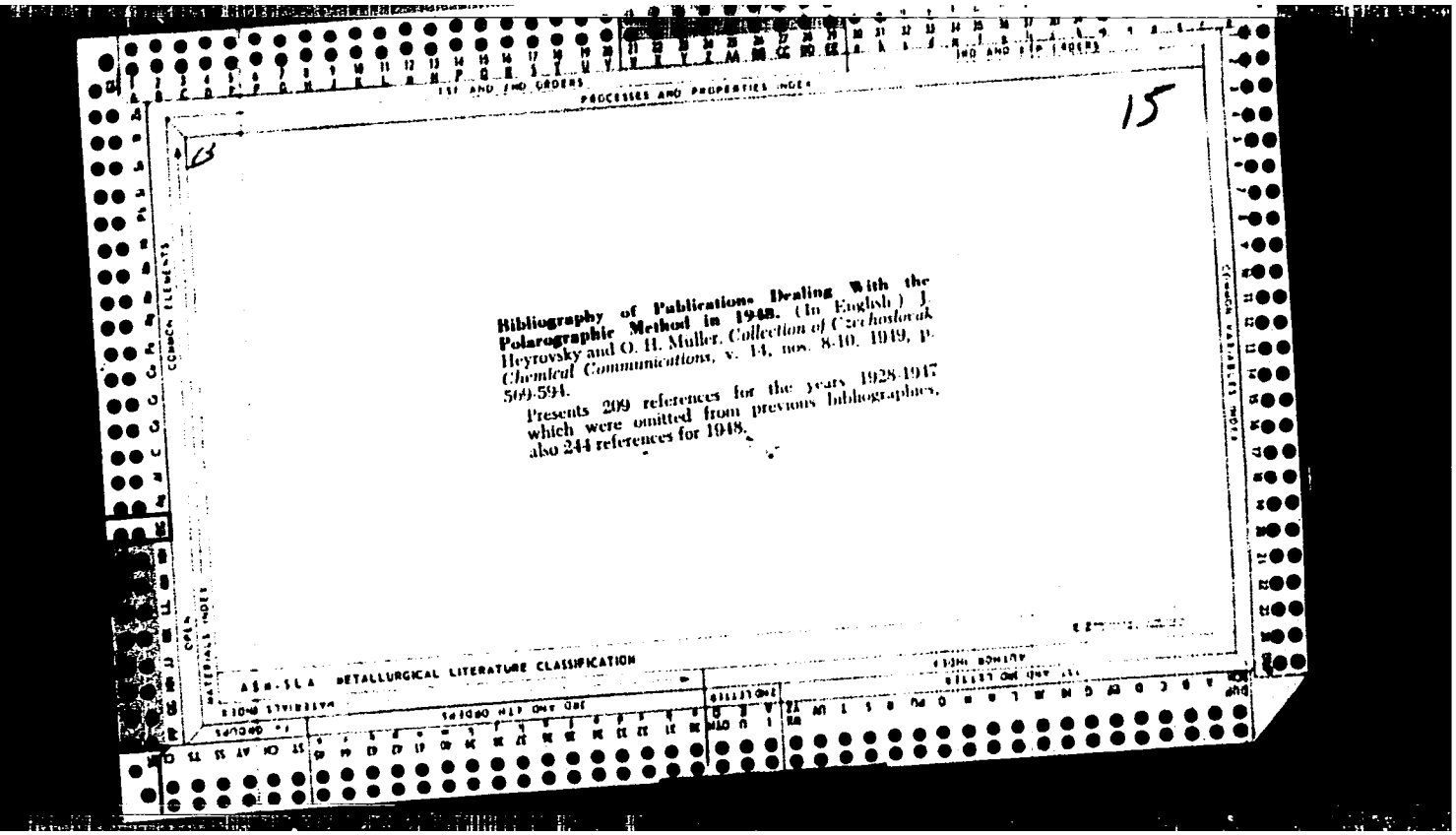

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The significance of derivative curves in polarography. J. Heyrovský. *Chem. Listy* **43**, 149–54(1949).—The deriv. curves first used in polarography were the oscillographic (dV/dt) – t curves showing the dependence of the differential quotient of the voltage (dV/dt) with respect to the time, t. They are used for analytical purposes and for the study of the rate of depolarization processes. Analogous diagrams can be automatically, and photographically registered showing the dependence of di/dE on E where 2 equal dropping electrodes are polarized. The difference between them, dE, being applied from a potentiometric bridge. The advantage of the polarographic derivative (di/dE – E) curve over the ordinary "primitive" current-voltage, i – E, curve are: at the half-wave potential the deriv. curve shows a max. the summit of which gives by its abscissa the quality (half-wave potential), and by the ordinate the quantity (a fraction of the diffusion current). The curve returns to zero at any diffusion current so that traces of the less-noble constituents are determinable in a large excess of the nobler ones. Complex waves composed of 2 or more almost coinciding waves are resolved by the deriv. into the components. Maxima of the deriv. curves due to the inflection point at the half-wave are well developed also when the primitive diffusion currents are indistinct. The deriv. maxima are on the whole more conspicuous than the waves of the primitive curves even when the depolarizers are greatly dild. The deriv. of the current-voltage curves with only one dropping electrode can be obtained: (1) by use of a condenser and galvanometer parallel to a resistance through which the electrolytic current flows; (2) by use of one galvanometer with 2 coils one of which indicates the current passing through it while in the other the deriv. di/dE is induced, which is shown by a second galvanometer; (3) by leading the primitive current into an induction coil which induces the derivative di/dE in the secondary coil. In the last 3 cases, the increase of the applied e.m.f., E, is supposed to be strictly proportional to the time so that $dE = Kdt$. The oscillographic (dV/dt) – V diagrams are analogous to ordinary polarograms yet show very minute differences between organic isomers such as *o*-, *m*-, *p*-nitrophenols, nicotinic, picolinic, and isonicotinic acids and nitrobenzene and *o*-, *m*-, and *p*-nitrotoluenes.

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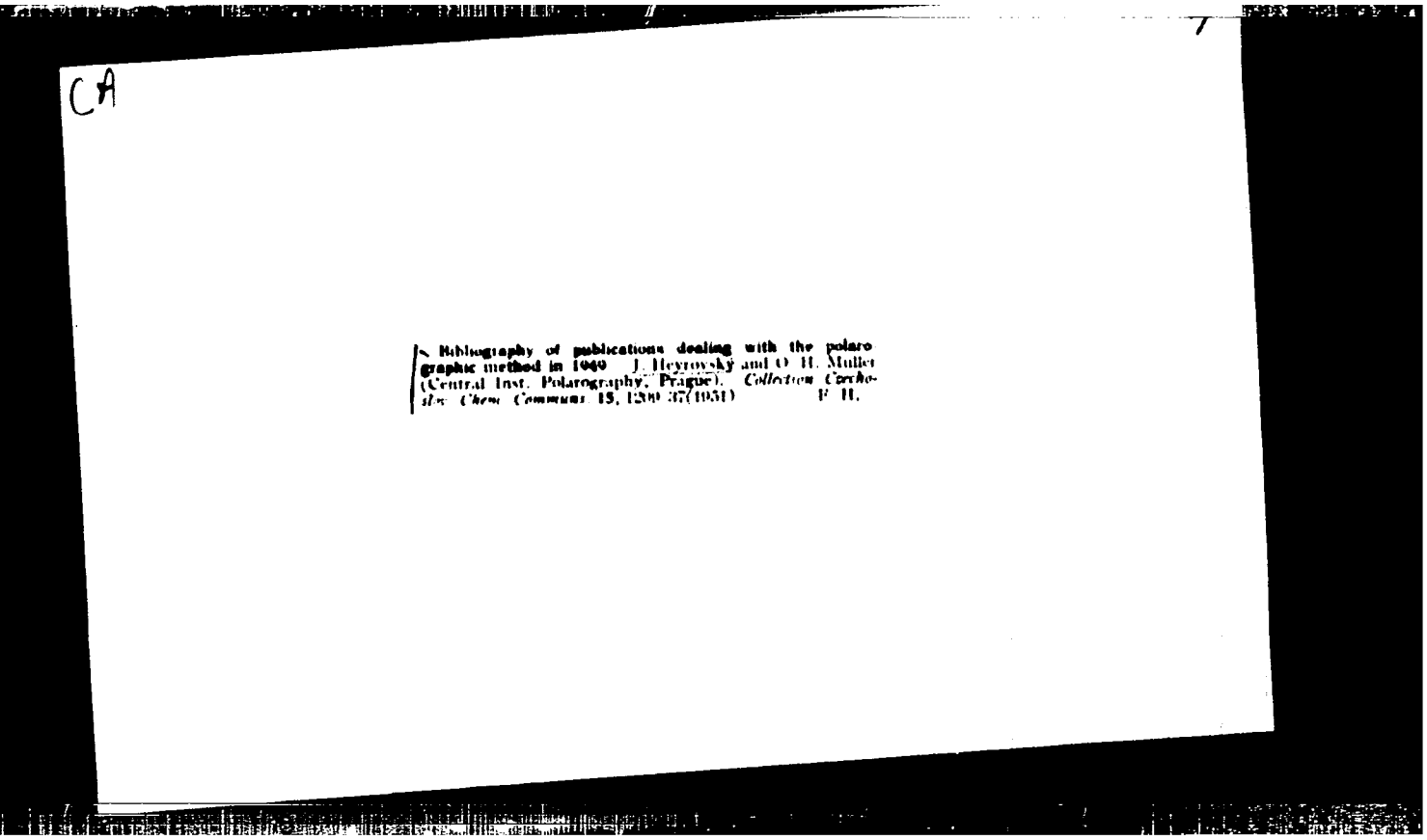

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24(2,4) PHASE I BOOK EXPLOITATION CZECH/2433

International Polarographic Congress. 1st, Prague, 1951

Sborník I. Mezinárodního polarografického sjezdu. Díl 3: Hlavní referaty prednesene na sjezdu. Proceedings...Vol 3: Reviews Read at the Congress. Praha, Přírodovědecke vyd-ví [1952] 774 p. 2,000 copies printed.

Resp. Ed.: Jiří Koryta, Doctor; Chief Ed, of Publishing House: Milan Skalník, Doctor; Tech. Ed.: Oldřich Dunka.

PURPOSE: The book is intended for chemists, chemical engineers, and physicists.

COVERAGE: The book is a collection of reviews and original papers read at the International Polarographic Congress held in Prague in 1951. Uses of polarography in organic and inorganic analysis, biochemistry, medicine, and industrial chemistry are discussed. In the section, Reviews Read at the Congress, Russian and either German or English translations of each review are presented. In the section, Original Papers Read at the Congress, only those translations in Russian, German, and English which

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have not been published in Volume I are presented. The following scientists participated in the opening of the Congress: Professor Wiltor Kemula, Dean of the Faculty of Sciences, Warsaw; Doctor Jaromir Dolansky, Minister of Planning; Professor Jaroslav Herovsky, Chairmen of the Congress; and Professor Jaroslav Fukatko, Chairman of the Center for Scientific Research and Technical Development. References follow each paper.

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